Swedish University of Agricultural Sciences
Department of Soil and Environment

Water purification capacity of natural mixed clays from Malawi

Anna Hernell

Master's Thesis in Soil Science
Agriculture Programme – Soil and Plant Sciences

Institutionen för mark och miljö, SLU
Examensarbeten 2009:01

Uppsala 2009

SLU, Swedish University of Agricultural Sciences
Department of Soil and Environment

Anna Hernell

Water purification capacity of natural mixed clays from Malawi

Supervisor: Ingmar Persson, Department of Chemistry, SLU
Assistant supervisor: Daniel Lundberg, Department of Chemistry, SLU
Examiner: Dan Berggren Kleja, Department of Soil and Environment, SLU
EX0429, Independent project/degree project in Soil Science, 30 HEC, Master D
Agriculture Programme – Soil and Plant Sciences (Agronomprogrammet – inriktning mark/växt)

Institutionen för mark och miljö, SLU, Examensarbeten 2009:01
Uppsala 2009

Keywords: chromium(III), lead(II), zinc(II), copper(II), cadmium(II), adsorption, surface complex, natural clays, water treatment

Abstract

Lack of fresh and clean drinking water is a problematic issue for many people worldwide. The water quality in some streams in Malawi, situated in south east Africa, has recently been investigated. The study shows that the concentration of several heavy metals exceeds the guideline values in drinking water set by WHO. Even though some heavy metals are essential for human beings in low concentrations, they are hazardous to health in high concentrations. Problems with contaminated water exist all over the world but are striking and more difficult to solve in countries with low financial assets. It is therefore of great importance to find an effective technique to purify water that is both simple and cheap and where preferably domestic material is used.

The aim of this study is to investigate whether three natural mixed clays from Malawi can be used to purify contaminated water from the heavy metals chromium(III), lead(II), cadmium(II), copper(II) and zinc(II) through adsorption.

X-ray powder diffraction analyses proved that all samples contained quartz, and indicated presence of the iron oxide hematite. The chemical content of the samples was determined with a scanning electron microscope. Acid and base titrations were thereafter performed on raw material as well as on clay that had been purified from organic matter, carbonates and iron compounds, to obtain information regarding the chemical properties of the clay minerals. Finally, adsorption experiments were carried out by mixing the clays with heavy metal solutions and study the adsorption as function of pH.

The pH values of the investigated clays are naturally high, which promotes hydrolyses of chromium(III) and lead(II) to precipitate and get sorbed on the surface. Cadmium(II), copper(II) and zinc(II) form on the contrary surface complexes, mainly inner-sphere ones. The adsorption of chromium(III), lead(II) and copper(II) was complete at pH = 7 for the purified clays, whereas cadmium(II) and zinc(II) were adsorbed to only 77 and 75 %, respectively, at pH ≈ 7.5. However, all metals are in principle completely removed from the aqueous phase in the raw material, which indicates that these non-treated natural clays are highly potential in heavy metal removal.

Keywords: *chromium(III), lead(II), zinc(II), copper(II), cadmium(II), adsorption, surface complex, natural clays, water treatment*

Sammanfattning

Att inte ha tillgång till rent dricksvatten är verklighet för många människor runt om i världen. En undersökning av vattenkvaliteten i några floder i Malawi, i sydöstra Afrika, visar att koncentrationen av ett flertal tungmetaller kraftigt överstiger de gränsvärden som världshälsoorganisationen WHO har slagit fast. Trots att vissa tungmetaller är livsnödvändiga i låga koncentrationer så kan de i för höga halter ha mycket negativa hälsoeffekter. Problem av dessa slag förekommer på många håll, men slår kanske hårdast mot de länder som har små ekonomiska tillgångar. Det finns därför ett stort behov av att utveckla en effektiv reningsmetod som är både enkel och billig och där inhemskt material kan nyttjas.

Denna studie syftar till att undersöka huruvida tre olika naturliga leror från Malawi kan användas för att rena kontaminerat vatten från tungmetallerna krom(III), bly(II), kadmium(II), koppar(II) och zink(II) genom adsorption.

Med hjälp av pulverröntgendiffraktion kunde det konstateras att alla prover innehåller kiseloxiden kvarts. Det fanns även tecken på att järnoxiden hematit förekommer. Proverna studerades i ett svepelektronmikroskop utrustad med röntgenfluorescensdetektor, vilket möjliggjorde bestämning av grundämnessammansättningen. Genom syra- och bastitreringar på råmaterial samt lera som renats från organiskt material, karbonater och järnföreningar erhölls information om lerytornas kemiska egenskaper. Slutligen genomfördes studier där lera blandades med tungmetallösningar och adsorptionsgraden undersöktes vid olika pH-värden.

Lerorna har naturligt ett högt pH-värde vilket främjar hydrolys av krom(III) och bly(II) som därmed faller ut och fastnar på ytorna. De andra studerade tungmetallerna, kadmium(II), koppar(II) och zink(II), adsorberades troligen till ytorna genom bildning av ytkomplex, främst av typen innersfärskomplex. Adsorptionen av krom(III), bly(II) och koppar(II) var fullständig vid pH = 7 i de renade jordarna, medan kadmium(II) och zink(II) endast adsorberades till 77 respektive 75 % i det undersökta pH-intervallet. I de orenade jordarna var däremot samtliga metaller i princip fullständigt avlägsnade från vattenfasen, vilket indikerar att dessa orenade naturliga leror har stor potential att kunna användas i vattenreningssyfte.

Nyckelord: *krom(III), bly(II), zink(II), koppar(II), kadmium(II), adsorption, ytkomplex, naturliga leror, vattenrening*

"… And chlorine, carbon, cobalt, copper, tungsten, tin, and sodium.
These are the only ones of which the news has come to Ha'vard,
And there may be many others, but they haven't been discover'd."

The Elements, Tom Lehrer (1959)

Table of contents

1 Introduction

1.1 Overview and background

Water is an invaluable resource, essential to all living organisms. For some of us, fresh and clean drinking water is always accessible just by turning on the tap, whereas scarcity of high quality water provokes serious health hazards to others (Mora *et al.*, 2009). Problems with contaminated water exist all over the world but are striking and more difficult to solve in countries with low financial assets. It is therefore of great importance to find an effective technique to purify water that in addition is both cheap and easily accessible.

The aim of this study is to investigate whether three different natural mixed clays from Malawi, Africa, can be used in order to remove five heavy metals (chromium(III), lead(II), cadmium(II), zinc(II) and copper(II)) from polluted water. All of these elements have a negative effect on human health if the intake is too high, keeping in mind that some of them are essential for human in small concentrations. In a recent study (Sajidu, 2008) the water quality of streams in Blantyre was investigated. Blantyre is the second biggest city in Malawi and a major commercial and industrial centre. Sajidu's study shows that the concentration of lead, cadmium, iron, manganese, chromium and nickel were higher (in some cases much higher) than the guideline values for drinking water set by the World Health Organization, WHO. Uncontrolled management of waste deposits is pointed out as one possible cause.

The focus of this study is on five heavy metals, where the concentrations of three of them in the examined streams in Malawi exceed the guideline values set by WHO, see Table 1.

Table 1. Guidelines for limit concentrations of heavy metals in drinking water set by WHO, concentrations of heavy metals in water samples from Malawi (c_{Malawi}) and concentration of heavy metals in simulated wastewater used in this study (c_{sw}).

heavy metal	WHO guidelines/mg/l	c_{Malawi} [a]/mg/l	c_{sw}/mg/l
Cr^{3+}	0.05[b]	0.013-0.479	400
Pb^{2+}	0.01	0.027-0.118	330
Cd^{2+}	0.003	0.002-0.015	310
Cu^{2+}	2	0.006-0.046	242
Zn^{2+}	3[c]	0.123-0.630	262

Source: WHO, 2006 and Sajidu, 2008.

[a] Lowest and highest mean value in water samples of three major streams in Blantyre City.

[b] Provisional because of uncertainties in the toxicological database.

[c] There is no guideline, but levels above 3 mg/l may not be acceptable to consumers.

The situation in Malawi is assumed to be representative for several countries in Africa and other developing countries worldwide. Hence, there is a need not only in this specific area for a simple, cheap and effective purification technique. Adsorption has been proven successful for removal of heavy metals from aqueous phases and clay minerals are excellent materials for adsorption (Bhattacharyya and Gupta, 2008). Even though numerous studies have been carried out with clay minerals as adsorbent, the majority have concerned modified clay minerals or one single clay mineral and not natural mixed clays. It is a great advantage if the required material can be found locally and used without any transformations, since it would reduce the costs and probably imply an increased utilization. Natural mixed clays are therefore preferable to modified clays. Studies of single phase systems are not adequate as basic data since they do not

describe the reality, nature is always much more complex than that. Knowledge provided by laboratory experiments of *natural mixed clays* is for that reason crucial in order to investigate its potential as adsorbent for heavy metals. Hopefully, these kinds of experiences can be the base for development of a simple, cheap and effective method that is applicable at a small-scale level.

Malawi is situated in south east Africa (see Fig. 1) and is one of the most densely populated countries in Africa. The total area of Malawi is 118 000 km^2, of which roughly a fifth is lakes and water courses. Malawi is landlocked and has a varying topography. Agriculture is the most important economical sector; it engaged 84 % of the economically active population in year 1998. The sector is mainly characterized by self-sufficiency farming. The BNP per capita was 2007 only 269 US dollar. One year earlier, the mean value for entire Africa was 670 US dollar per capita (Nationalencyklopedin, 2009a).

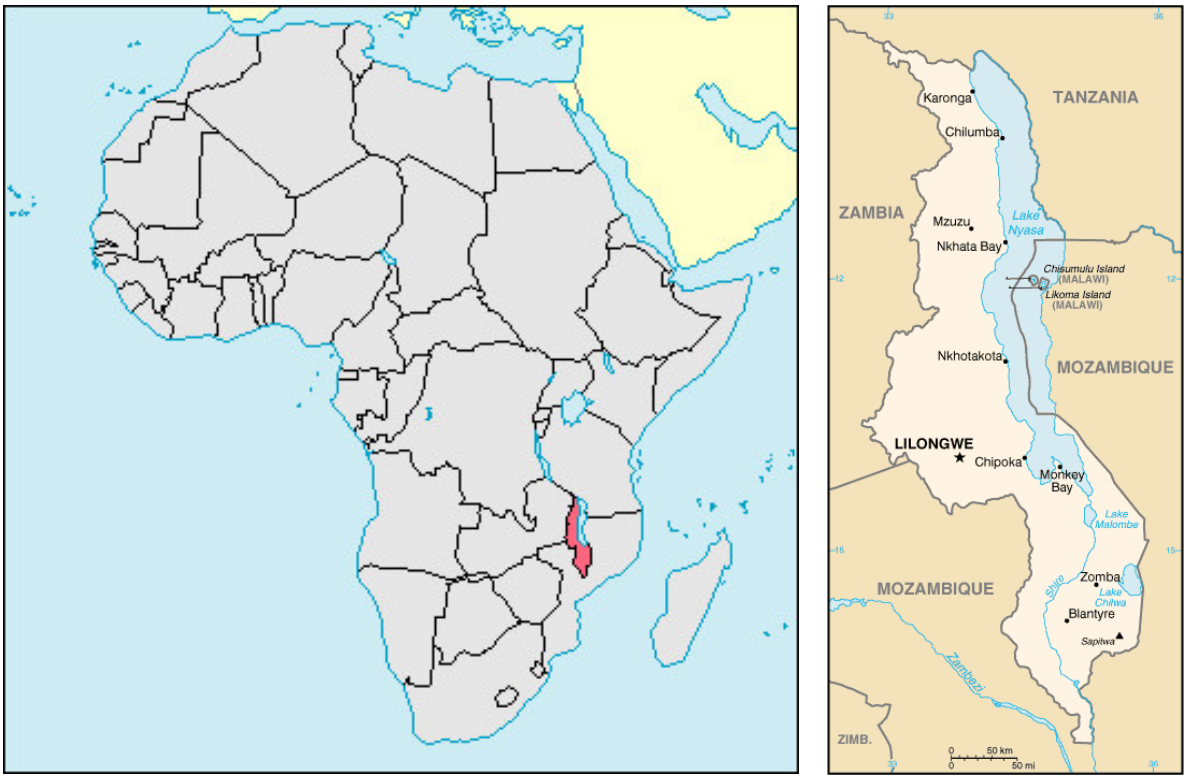


Figure 1. Malawi is marked in red on the map of Africa. The picture to the right shows Malawi and its surrounding countries. From Nationalencyklopedin (2009a) and Wikipedia (2009a) respectively.

1.2 Objective

The objective of this study is to examine the chemical and physical properties of three different natural mixed clays from Malawi and investigate whether they can be utilized to remove five specific heavy metals (chromium(III), lead(II), cadmium(II), zinc(II) and copper(II)) from polluted water through adsorption.

1.2.1 Aim

- Perform physical-chemical experiments to determine whether the studied soils can be used for cleaning of contaminated water.
- Determine to which extent the heavy metals are adsorbed as function of pH.
- What kinds of complexes are formed? Is the process reversible or irreversible?

1.2.2 Disposition

A brief introduction to the subject is presented in Chapter 2. Thereafter is the laboratory experimental part of the study described. The three examined clays were purified from carbonates, iron compounds and organic matter in order to determine their mineral composition and to get a less sprawling and ambivalent picture of the clays. If a sufficiently large amount of clay was available, experiments were performed on purified clay as well as on the raw material.

2 Literature review

This Chapter aims to give a basic understanding of heavy metals, clay minerals and the adsorption processes that may occur on the interface between the solid phase and the soil solution. Some techniques for mineral characterization are also described.

2.1 Heavy metals

The expression *heavy metal* is commonly used, and my guess is that one does not need long time of consideration to relate it to something. One might associate it to batteries, metals hazardous to health or even rock music! In this study the focus is on five specific heavy metals, and their potential toxicological effects and biological function will be briefly discussed in this Chapter.

2.1.1 Definition

The term heavy metal has been widely used. There is, however, no general agreement on which elements that are meant to be included in the expression, and no authoritative definition of heavy metals exists (Duffus, 2002). Still, it is often used to describe a group of metals and semimetals associated with pollution and potential toxicity or ecotoxicity. This is not an accepted fact and the term heavy metal is for that reason misleading and confusing (Duffus, 2002). Due to lack of a better classification, the term is still utilized. The definition used in this study describes heavy metals as a metal with a density higher than 5000 kg/m^3, unlike light metals which have a lower density. With this definition most of the metallic elements belong to the group heavy metals, see Fig 2.

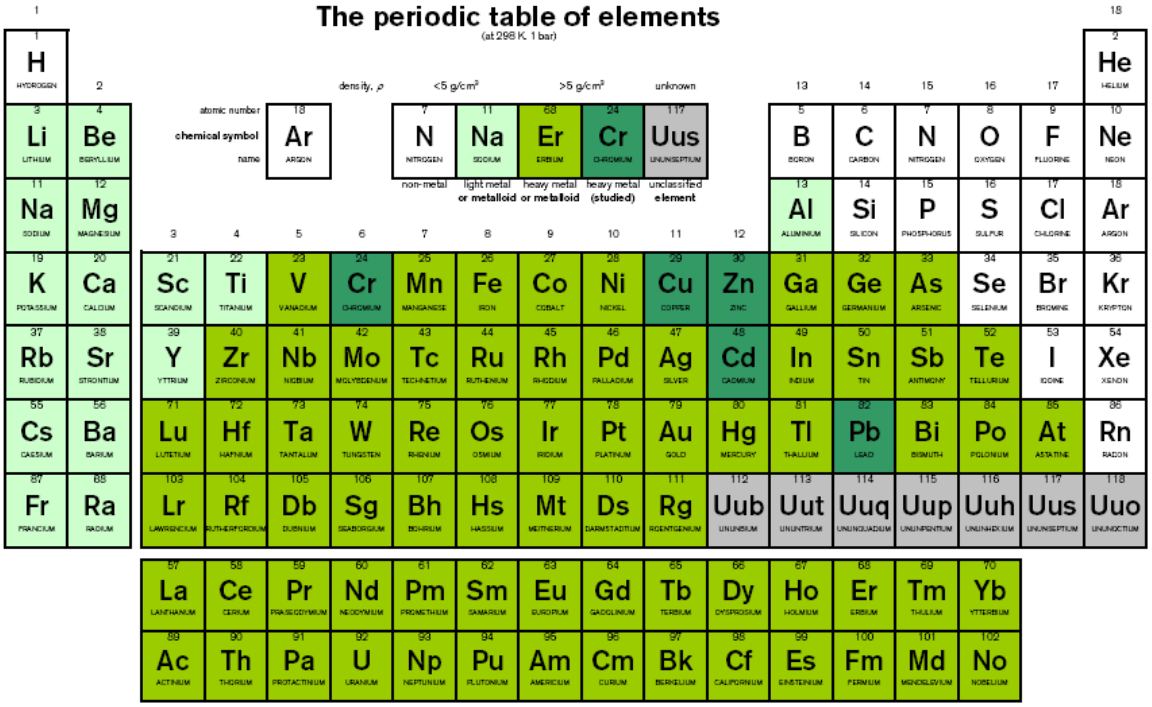


Figure 2. The periodic table of elements. Heavy metals are colored green, the five of interest in this study are dark green. Light metals are light green.

2.1.2 Toxicological effects and biological function

As mentioned above, there is no given correlation between the density of a metal and its toxicity. Many light metals and light metal compounds can also be strongly toxic and/or affect the environment negatively. However, most of the heavy metals, their ions, and their chemical compounds *are* toxic, but it is important to remember that many heavy metals on the contrary are essential for humans, animals and plants (Nationalencyklopedin, 2009b).

In this study, laboratory experiments have been carried out with the five following heavy metals, lead(II), cadmium(II), chromium(III), zinc(II) and copper(II). Neither lead nor cadmium ions have a positive biological function, their chemical compounds are toxic. Lead is transported by the blood and enriched in liver, kidneys and spleen, and can thus harm these organs. Intake of water-soluble lead salts can cause acute poisoning with symptoms such as tiredness, stomach trouble, anaemia and disturbances in the central and peripheral nervous system. Cadmium compounds are toxic to all living organisms in higher doses or concentrations. It can be enriched in kidneys and liver and is also likely to be carcinogenic (Nationalencyklopedin, 2009c).

On the other hand, chromium, zinc and copper are examples of heavy metals whose ions, in relatively low concentration, are essential for life. In humans, chromium ions are involved in the utilization of glucose while copper and zinc ions are components of several enzymes. Intake of higher amounts of copper compounds can however lead to acute poisoning with vomiting and diarrhoea as a consequence and chromium(VI) compounds can give rise to skin allergy (Nationalencyklopedin, 2009d).

2.1.3 Conventional methods for retention of heavy metals

Several different techniques are used for removal of heavy metals from wastewater. Chemical precipitation, electrolysis, reverse osmosis, solvent extraction, ion exchange, sand filtration and adsorption are all utilized with this intention (Sajidu, 2008; Eren, 2008). Adsorption refers to the process where material bind to a surface, and must be distinguished from absorption where material or an energy form penetrate and get enclosed by a substance, see Fig. 3. The solid phase involved in adsorption is named adsorbent whereas the matter that is accumulated on the interface is called adsorbate.

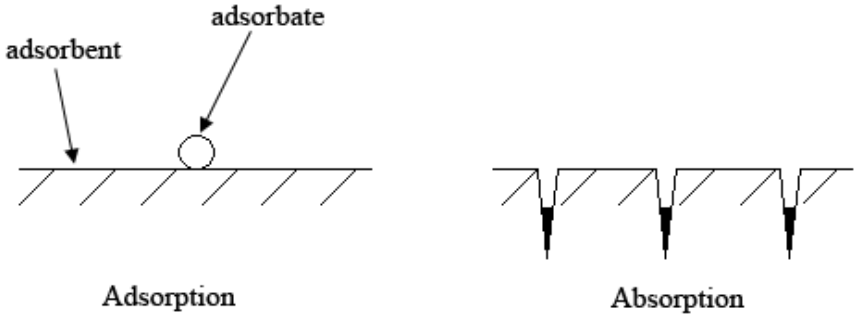


Figure 3. Adsorption and absorption.

A recent study (Bhattacharya *et al.*, 2006) showed that adsorption was successful for retention of heavy metals; it is highly effective and easy to adapt at low costs. Studies have been carried out with for example activated carbon, clarified sludge and different clay minerals as adsorbent. Clay minerals possess many properties that make them effective for removal of metal ions of aqueous solutions. They have for instance high specific surface area, high chemical stability, layered structure and high cation exchange capacity (Bhattacharya *et al.*, 2006). The abundance of clay minerals and their low cost are additional factors making them potentially very suitable for this purpose. Even though numerous studies have been carried out with clay minerals as adsorbent, the majority have concerned modified clay minerals or one single clay mineral and not *natural mixed clays* which is the case in this thesis. However, in previous studies at the department of chemistry, SLU, Uppsala, natural mixed clays from Malawi and Mali, respectively, have been investigated (Sajidu, 2008 and Sällström, 2008).

2.2 Soil mineral

About one-half to two-thirds of the volume of a soil is made up by solid matter. Inorganic compounds represent often more than 90 % of the solid phase, except for peat and muck soils where the share of organic matter is extremely high (more than 50 %). Despite the fact that inorganic solid phases in soils are very diverse, a number of different solid phases of fairly uniform composition (i.e. minerals) have been identified in soils all over the world (Sposito, 1989).

Minerals are divided into primary and secondary minerals. The primary ones are derived from rocks that have been transformed to deposits through physical weathering. These minerals are chemical unstable in the soil environment and will therefore begin to decompose (Eriksson *et al.*, 2005). The mineral products of this chemical weathering of primary minerals are referred to as secondary minerals, which have a lower solubility than the primary ones (McBride, 1994).

2.2.1 Primary minerals

Primary minerals are mainly silicates. The corners of the silicate unit (SiO_4-tetrahedron) can be shared and a number of different geometrical arrangements can be formed. They are named island, chain, layer and framework silicates. The negative charge of the silicate ion is compensated by cations distributed in the structure. Quartz is an example of a framework silicate. Each oxygen binds to two silicon atoms and the mineral is therefore very hard and resistant to weathering (Eriksson *et al.*, 2005). Furthermore, olivine is an island silicate, pyroxenes are chain silicates and mica is one example of layer silicates (McBride, 1994).

2.2.2 Secondary minerals

Secondary minerals primarily constitute of layer silicates, allophanes and imogolite (non crystalline silicates) and oxides and hydroxides of iron and aluminum (McBride, 1994; Eriksson *et al.*, 2005). The term *clay mineral* is frequently used for secondary minerals since they often belong to the clay fraction, i.e. their grain size is <0.002 mm (Eriksson *et al.*, 2005). Primary minerals whose particles are of clay size belong to the clay fraction as well, but they are not classified as clay minerals (McBride, 1994).

Three different structural types of layer silicates exist: 1:1, 2:1 and 2:1:1 silicates, see Fig. 4. In 1:1 layer silicates, e.g. kaolinite, each individual layer is constructed from one tetrahedral sheet and one octahedral sheet. The latter one consists of oxygen and hydroxide ions together with cations in the octahedral cavities. In 2:1 silicates, an octahedral sheet is surrounded by two tetrahedral sheets. Illite, vermiculite and smectite are all examples of this kind of layer silicates. However, these minerals have a varying grade of isomorphic substitution (the term is explained in Chapter 2.2.3). Furthermore, chlorite is a 2:1:1 mineral, it is built up like a 2:1 mineral but there is an extra octahedral oxide/hydroxide sheet in between the structure (McBride, 1994).

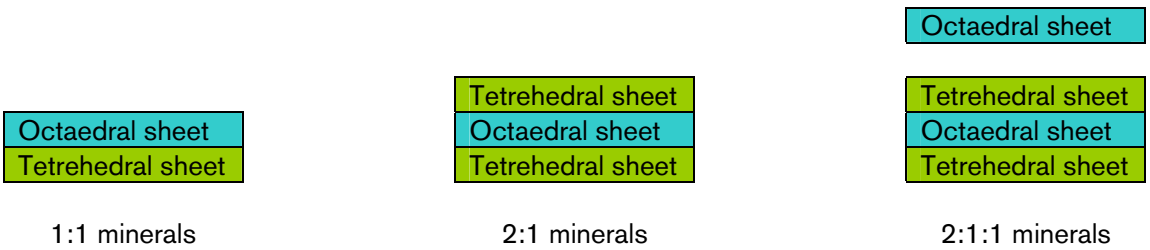


Figure 4. Schematic packing of sheets in clay minerals.

2.2.3 Surface charge

Solid-particle surfaces in soils develop electrical charge in two different ways (Sposito, 1989). *Permanent structural charge* arises when cations built-in in the structure, to neutralize charge deficit due to isomorphous substitution, are removed through weathering. Isomorphous substitution is a replacement of an ion in the structure by another one of equal size but with lower valency (Eriksson *et al.*, 2005). These negative charges can be found in primary as well as secondary minerals, but are of considerable size only in 2:1 minerals (Sposito, 1989).

The second type of charge changes with pH and is therefore named *variable charge*. These charges exist on all kinds of colloidal particles and can be both positive and negative. OH groups on edges of clay minerals act as weak acids or bases and can dissociate or take up a proton depending on the pH of the surrounding solution. The reactive functional groups on organic matter are mainly carboxylic groups, -COOH, but also hydroxyphenyl groups, $-C_6H_4OH$, alcoholic OH and amino groups, $-NH_2$ (Eriksson *et al.*, 2005; Stumm, 1992). See Chapter 2.4 for a more detailed description of the behavior of variable charges on mineral surfaces.

Nature seeks to counterbalance charge. Any charges on particle surfaces will therefore be balanced in one way or another. Due to electrostatic attraction, a surplus of ions of opposite charge than the surface will be present close to the surface. In the same area, repulsion causes a deficit of ions of same charge. These ions are movable and can be replaced by another ion, and are for that reason named exchangeable (Eriksson *et al.*, 2005). In addition, surface complexes can be formed, which are studied in this thesis.

2.3 Mineral characterization

Solid compounds are either crystalline or amorphous. Crystals possess long-range order, which implies that their atoms, ions or molecules are arranged in a well-organized structure that is repeated exactly in all three dimensions at a great distance. On the contrary, there is a short-range order of the atoms, ions or molecules in amorphous compounds which also is the case for liquids. Nevertheless, amorphous compounds are solids but the atoms, ions or molecules do not occupy specific positions in a regular pattern as in crystals (Chang, 2005).

2.3.1 X-ray powder diffraction (XPD)

In order to identify an unknown compound, information regarding the arrangement of its constituents is needed. If the structure of a crystal is to be determined, only detailed knowledge of the unit cell, i.e. the smallest building block, is required for complete description. X-ray diffraction is an accurate and applicable method when it comes to structural analyses of unknown *crystalline* solids. Bond lengths and bond angles can be determined as well as the distance between the layers of atoms and the centering of the unit cell. When comparing this obtained information with a reference database the crystalline compound can be identified.

The X-ray diffraction technique is based on the following principle. A metal is bombarded with high energy electrons. Some of the incoming electrons will interact with the electrons in the metal and these electrons will consequently be pushed out. When an electron located further out from the nucleus falls into the vacancy the energy excess is emitted as an X-ray photon with very well defined energy (wave-length). The

created X-rays are directed towards the studied crystal whose electrons cause the X-rays to be scattered. X-rays behave as waves that interfere with each other, i.e. waves in phase reinforce each other while waves out-of-phase weaken each other. A reflection is formed only when the reflected X-rays are in phase with each other. In other words; Bragg's law (given below) must be satisfied (Atkins, 1996).

$$n\lambda = 2d \sin\theta \quad \text{(Bragg's law)}, \qquad \text{Eq. 1}$$

where n is an integer, λ is the wavelength of the X-rays, d is the distance between the Miller layers in the structure and θ is the angle of the incident X-rays. The reflected beams are in phase if the extra distance (BC + CD) traveled by the lower wave is an integer multiplied with the wavelength of the X-ray, see Fig. 5.

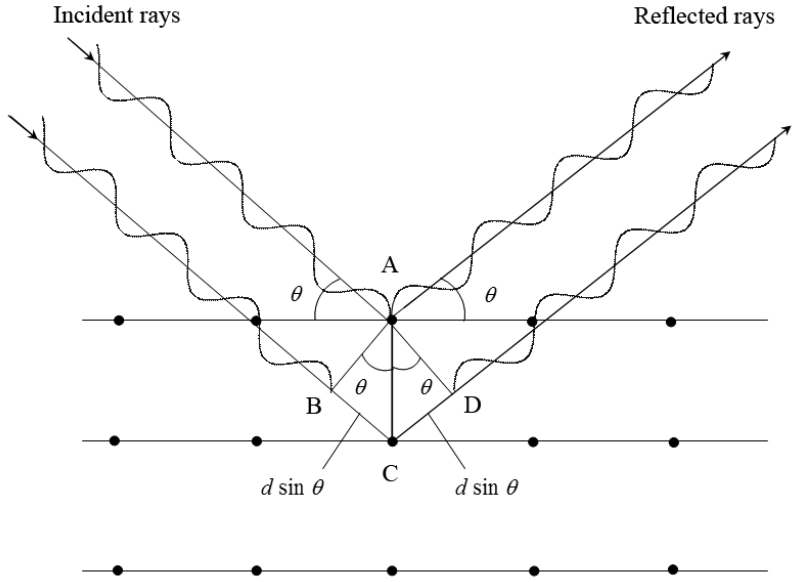


Figure 5. Reflections of X-rays from two layers of atoms (after Chang, 2005). The horizontal lines represent Miller layers.

If the studied sample is not completely crystalline, thus amorphous, no *distinct* reflections will be generated. A related method is therefore used, X-ray powder diffraction. It is based on the same principle as X-ray diffraction and the same equipment can be used. When the sample is a powder, some of the crystallites or micro-crystallites will always be located in such a way that Bragg's law is satisfied and diffraction patterns will consequently be created at different incident angels (Atkins, 1996). X-rays hitting a powder sample will not cause a diffraction pattern with distinct dots, instead the diffracted beam from each plane of atoms give rise to a ring. This ring pattern is interpreted by a software program and converted into a diffraction pattern where the intensity is plotted against the scattering angle, 2θ. Every substance has its own unique powder diffraction pattern that can be used as a "fingerprint". Thereby, a comparison with known reference diffraction patterns may lead to identification of an unknown compound (Nationalencyklopedin, 2009g). In addition, with this method it is possible to decide whether the compound is crystalline or not. Even though X-ray powder diffraction does not originate as much detailed information as single crystal X-ray diffraction, it is still a very easy and fast method, where different crystalline and micro crystalline compounds (e.g. soil minerals) can be identified and characterized.

2.3.2 Scanning electron microscopy (SEM)

An electron microscope, as well as a normal light microscope, produces an enlarged image. However, in an electron microscope, the sample is illuminated with electrons instead of light photons. According to the law of optics, it is not possible to create an image of an object smaller than half of the size of the wavelength that is used (Chang, 2005). When the sample is illuminated with electrons with a shorter wavelength than visible light, a higher magnification can consequently be achieved. It is possible to magnify an object up to 500 000 times in an electron microscope compared to 2 000 times in a light microscope (ALS Laboratory Group, 2009). The equipment used in this study can accomplish a 10 000 times enlarged image.

In this study, a scanning electron microscope (SEM) was utilized, which is the most commonly used type of electron microscopes (Nationalencyklopedin, 2009e). A beam of electrons is scanning the sample and the emitted electrons are detected. From these data, an image of the surface is created. Hence, the surface and the appearance of the particles can be explored.

If the SEM device is equipped with an energy dispersive X-ray fluorescence detector (EDS or EDX) it is also possible to determine the chemical composition of elements heavier than neon ($Z > 10$) in the sample. When an electron in the sample is hit by an incoming high energy electron it is kicked out and a vacancy is created just as described in Chapter 2.3.1. An electron located further out from the nucleus drops into the vacancy and the energy excess is emitted as an X-ray photon. Every single element emits X-rays of a specific energy. Hence, it is possible to determine the chemical composition with great accuracy of elements with $Z > 10$. Both amorphous and crystalline elements are detected with this technique, whereas X-ray diffraction only recognizes crystalline phases.

2.4 Surface chemistry

Important chemical processes take place on the interface between the solid phase and the soil solution. These processes affect, among all, the accessibility of nutrients to plants and control the solubility of various compounds. A change of pH level can cause a state of equilibrium to be shifted in one or another direction. Elements bound to a surface might as a result be released in a very short period of time. Furthermore, elements can be released through weathering, but this is a much more time-consuming process (Eriksson *et al.,* 2005).

2.4.1 Surface complexation

After contact with water, a mineral surface will consist of ≡M-OH groups, where ≡M-O illustrates an oxide surface, with M being its central ion. H is an attached hydrogen ion. M can represent a metal ion as well as a silicon ion, which is the case for e.g. quartz. The bond between oxygen and silicon is however very covalent, i.e. there is a great overlap of electrons and the charge neutralization is high. The charge of oxygen is therefore almost non-existing and no cations will be attached to it. The silica group can be considered as a very strong acid that deprotonates very easily. Hence, a quartz surface in contact with water looks like $\equiv Si\text{-}O^-$ and not ≡Si-OH.

The ≡M-OH groups are amphoteric, which means that they are able to act as both acid and base (McBride, 1994) and thus form ≡M-O^- or ≡M-OH_2^+ surface sites. The total concentration of surface sites is therefore given by the following expression:

$$\{\equiv M\text{-}OH_{tot}\} = \{\equiv M\text{-}OH_2^+\} + \{\equiv M\text{-}OH\} + \{\equiv M\text{-}O^-\} \quad \text{Eq. 2}$$

$\{\equiv M\text{-}OH_2^+\}$ is regarded as a diprotic acid with the following dissociation steps and acidity constants:

$$\equiv M\text{-}OH_2^+ + H_2O \rightleftharpoons \equiv M\text{-}OH + H_3O^+, \quad \text{Eq. 3a}$$

where the first acidity equilibrium constant $K^s_{a1,app}$ is defined as

$$K^s_{a1,app} = \frac{\{\equiv M\text{-}OH\}[H_3O^+]}{\{\equiv M\text{-}OH_2^+\}} \quad \text{Eq. 3b}$$

Similarly, for the second dissociation step

$$\equiv M\text{-}OH + H_2O \rightleftharpoons \equiv M\text{-}O^- + H_3O^+, \text{ where} \quad \text{Eq. 4a}$$

$$K^s_{a2,app} = \frac{\{\equiv M\text{-}O^-\}[H_3O^+]}{\{\equiv M\text{-}OH\}} \quad \text{Eq. 4b}$$

The curly brackets, {}, denote the concentration of a substance bound to the surface while the square brackets, [ ], denote a concentration of a substance in solution.

The acidity constants, $K^s_{a1,app}$ and $K^s_{a2,app}$, can be determined based on data obtained from acid and base titrations. Index s illustrates that the material is solid, and app stands for apparent. When these constants are known, pK_a values, i.e. the negative logarithmic form of the acidity constant, and thereby also the pH_{pznpc} (see explanation further down) can be calculated. All together, these terms give a fundamental knowledge about the studied mineral and facilitate the understanding of the adsorption processes taking place on the mineral surface.

Point of zero net proton charge (pznpc) is the pH value at which the amount of ≡M-OH_2^+ groups is equivalent to the amount of ≡M-O^- groups. On the contrary, when considering the total charge of the particle, *point of zero charge* (pzc) is used. This refers to the pH value at which the net surface charge is zero; *all* positive and negative charges are of equal size. In this study, only the proton balance has been investigated and no information about any potential permanent charges is available, hence the concept of pznpc is used instead of pzc. There is also a third concept, *point of zero net charge* (pznc), where the net adsorbed ion charge, other than that caused by deprotonization and protonization, is zero (Sposito, 1989).

The net charge of the surface varies with the level of pH and will be negatively charged when the pH level in the surrounding solution is higher than pH_{pzc}, as a result of the withdrawal of protons from the surface caused by hydroxide ions in the solution for the formation of water. On the other hand, a pH lowering implies a higher concentration of hydrogen ions. The amount of positively charged sites on the surface will increase and the net charge will consequently be positive. This is clearly shown in the association

reaction below which will shift to the right at an increased concentration of hydrogen ions:

$$\equiv\text{M-OH} + \text{H}_3\text{O}^+ \rightleftharpoons \equiv\text{M-OH}_2^+ + \text{H}_2\text{O}, \text{ where} \qquad \text{Eq. 5a}$$

$$K_{\text{ass}}^{\text{s}} = \frac{\left\{\equiv \text{M-OH}_2^+\right\}}{\left\{\equiv \text{M-OH}\right\}\left[\text{H}_3\text{O}^+\right]} = \frac{1}{K_{\text{a1,app}}^{\text{s}}} \qquad \text{Eq. 5b}$$

As the surface becomes more and more positively charged, further addition of hydrogen ions to the surface will be aggravated due to the repulsion that merge when particles of same charge get close to each other. In consequence, the association reaction above will not be shifted as much to the right as before and the association stability constant K_{ass} decreases. On the contrary, the acidity constant, K_a, increases since it is the inverse of K_{ass}. The common logarithm of K_a, named pK_a, decreases thereby as the surface becomes more and more positively charged.

$$\text{p}K_a = -\log_{10} K_a \qquad \text{Eq. 6}$$

2.4.2 Adsorption

Adsorption occurs on the interface between a solid phase and an aqueous solution and comprehends a net accumulation of matter (Sposito, 1989).

2.4.2.1 Adsorption of metal ions to mineral surfaces

Three different types of bonding characteristics for adsorption on soil particle surfaces exist. This is illustrated in Fig. 6. The most stable one is called inner-sphere surface complex, where the adsorbate is not surrounded by a full hydration shell and directly and specifically bound to a surface group on a particle. The bonding is mainly covalent; an electron pair is shared between the adsorbed ion and the atom in the surface. The adsorbed ion is considered to be a part of the surface and is not regarded as readily exchangeable. However, it can slowly be released depending on the chemical condition in the aqueous solution (Eriksson *et al.,* 2005).

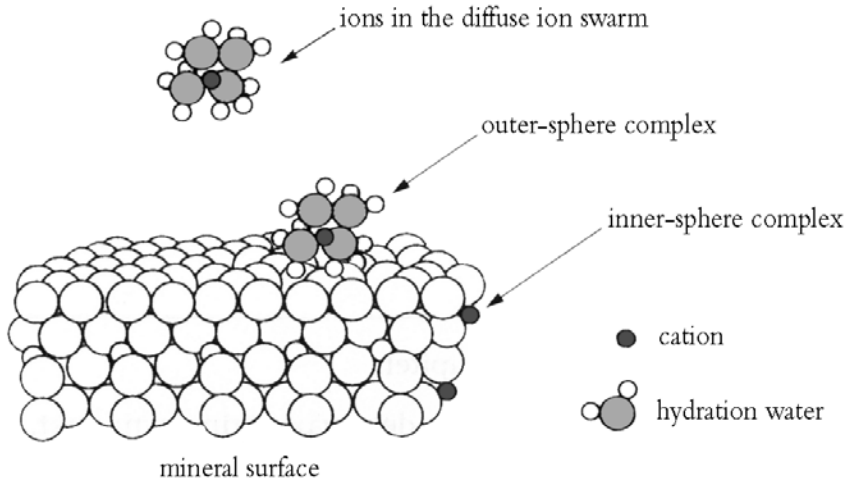


Figure 6. Cation adsorption through inner-sphere surface complex, outer-sphere complex and exchangeable ions in the diffuse-ion swarm. Modified from Eriksson *et al.*, 2005.

Outer-sphere complex is the second type of adsorption mechanism. The ion is not localized to a specific spot on the surface and it is still surrounded by its hydration shell. Electrostatic interactions keep the ion in place instead of covalent bonding. In a soil, inner- and outer-sphere complexes can be formed with surface groups with variable charges, i.e. ≡Fe-OH and ≡Al-OH groups on mineral colloids and carboxyl and phenol groups on humus (Eriksson *et al.,* 2005).

The third mechanism, which is called the diffuse-ion swarm, includes solvated ions neutralizing the surface charge without forming any true complexes. Likewise outer-sphere complexes, ions in the diffuse-ion swarm are kept in place by electrostatic bonding to the charged surface. Furthermore, ions adsorbed through outer-sphere complexes or in the diffuse-ion swarm are as mentioned fully solvated and consequently defined as readily exchangeable (Sposito, 1989). The only difference between these two adsorption mechanisms is that ions in the diffuse-ion swarm are localized further out from the surface than outer-sphere complexes.

2.4.2.2 The pH level of the surrounding solution affects adsorption

Cations can be adsorbed to a surface even when it is positively charged, i.e. $pH < pH_{pzc}$. It forms then inner-sphere complexes. The ions are attached to the surface through specific bonding and adsorption is not dependent of electrostatic forces to occur. The same argument is valid for anions but with the difference that they form inner-sphere complexes if they are able to adsorb to a negatively charged surface, i.e. $pH > pH_{pzc}$. On the contrary, if adsorption requires a surface with a net charge that is of the opposite kind than the ion itself, an outer-sphere complex is formed (Stumm, 1992).

2.4.2.3 Adsorption affects pH_{pzc}

Formation of surface complexes with cations shifts pH_{pzc} to a higher value, whereas adsorption of anions generates a lower pH_{pzc} (Sposito, 1989). The adsorbed cation and its charge becomes a part of the mineral surface, which implies that pH_{pzc} increases. With other words; a higher pH is required so as to neutralize the increased amount of positively charged sites and get a neutral surface.

2.4.3 Extended X-ray absorption fine structure (EXAFS)

EXAFS is used to characterize e.g. sorbed metal ions on the clay surface (Sajidu, 2008). The sample is exposed to X-rays of very high intensity which interfere with the electrons closest to the core of the atoms. This generates information about the distances between the absorbing atoms and their neighbours (Jalilehvand, 2000). When the distances are known, the structure can be evaluated. The EXAFS technique requires however X-rays of extremely high intensity. At MAX-lab at Lund University, where the analyses were carried out, X-rays of the intensity 10^{14} photons/s·mm^2 are produced. Electrons travels with the speed of light in a storage ring and are forced to turn by strong magnets, and thereby be accelerated. When charged particles accelerate intense electromagnetic radiation in a wide spectrum is formed. The obtained electromagnetic rays, e.g. X-rays, are collected in a beam-line and focused towards the sample.

3 Materials and methods

In this thesis, soil samples from three different locations in Malawi have been studied. The soils are called Namadzi clays, Linthipe ceramic clays and Za mkt clays; they are referred to as Nc, Lcc and Zmc respectively in the text. When only these abbreviations are used it alludes to the purified samples, whereas for example "Nc raw" refers to non purified material.

3.1 Origin of the soil samples

The Nc raw sample is collected near a small township called Namadzi in the Chiradzulu district (see Fig. 7), which is located in the southern part of Malawi. Clay pots are manufactured by this clay. Since the pots have a cooling effect, they are commonly used for storage of drinking water in villages where electricity is not available.

The Lcc raw sample is collected from a place called Linthipe in the Dedza district in the central region of Malawi. The clay is used when making ceramics for water storage. In addition, it is utilized in ornaments and moulding statues.

The Zmc raw sample is collected at a spot about 100 meters from the market in Zomba, which is a town but also the name of the district in the southern part of Malawi. People, mostly women from the rural areas, come to get this clay and use it for cleaning of kitchen wares.

Figure 7. Map of Malawi where the capital town Lilongwe is marked with a red dot. Number 1 denotes the Dedza district whereas number 2 and 3 denotes Zomba and Chiradzulu district, respectively (after Wikipedia 2009b).

3.2 Sample sifting

An automatic sieve (Retsch Vibro) was used to sift the soil samples yielding five fraction sizes, f_n, were received: $f_1 < 0.032$ mm, $0.032 < f_2 < 0.045$ mm, $0.045 < f_3 < 0.063$ mm, $0.063 < f_4 < 0.125$ mm, and $0.125 \text{ mm} < f_5$. The nets in the sieve were carefully cleaned when switching to another sample by putting them in an ultrasonic bath and thereafter dry them with acetone and a hair-drier. For Nc raw and Lcc raw, particles with the following sizes were used in the purification process: $0.032 < f < 0.063$ mm. When it comes to Zmc raw ($0.032 < f < 0.125$ mm), bigger particles had to be included in order to get a sufficiently large soil sample.

3.3 Sample purification

Even though this study aims at investigating to which extent natural mixed clay can be used for heavy metal removal, the soil samples need to be purified in order to determine their mineral composition. Otherwise, impurities such as carbonates, iron and organic matter may distract and aggravate the mineralogical analyses (Sajidu, 2008). Presence of carbonates in the clay may result in indistinct X-ray powder diffraction pattern and also reduce the efficiency of hydrogen peroxide, which is used for removal of organic matter. Organic matter binds to mineral surfaces, and may thereby hide the properties of the mineral. Iron oxides impede the possibility to disperse clay; their coverage of mineral particles makes the particle separation more difficult (Sajidu, 2008). Another reason for purification is that raw clay comprising organic matter would provide a much more sprawling depiction of its properties since organic matter consist of a less homogenous composition than inorganic surfaces.

The purification procedure was carried out as described in Sajidu (2008) and references therein, and is designed in order to get rid of impurities without affecting the actual constituents of the clay mineral more than necessary. Potential carbonates were removed by addition of sodium acetate-acetic acid buffer, since acid causes carbonates to decompose under formation of gaseous carbon dioxide. In the iron purification step a strong reducing agent (sodium dithionite) and sodium citrate dihydrate, which forms strong chelate-complexes with both Fe^{3+} and Fe^{2+}, were added. These two compounds increase the solubility of iron. The complex formation between citrate (in the base form) and iron requires a basic medium, an adjustment was therefore done with sodium hydroxide to get pH = 8.3. Addition of sodium hydrogen carbonate aims at stabilizing the pH. In order to remove organic matter from the clay, hydrogen peroxide was used. Hydrogen peroxide is a strong oxidation agent which oxidizes the carbon and the organic matter is consequently decomposed (Chang, 2005). Its maximum effect is achieved in acidic medium; acetic acid-sodium acetate buffer was therefore added as well. Hydrogen peroxide readily decomposes at high temperatures; the suspensions were therefore heated to 90 ºC. The purification procedure is briefly described in Chapter 3.3.1-3.3.3, more information can be found in Sajidu (2008). Precise masses of weighed clays and volumes and masses of different additions are given in Appendix 1.

Some analyses were carried out on raw clay as well as on purified clay. Small shares (5-10 g) of each soil sample were therefore not treated in the purification processes.

3.3.1 Removal of carbonates

Raw clay (80-100 g) was dispersed in 1.0 M sodium acetate-acetic acid buffer. The relation was initially 1 g clay to 1 ml buffer, according to Sajidu (2008). The suspensions

were put on magnetic stirrers to accelerate the carbonate decomposition. After three days the samples had dried and distilled water was added to regain the suspensions. The formation of carbon dioxide bubbles did end after six days, hence the samples were assumed to be free from carbonates. The solutions were washed with distilled water five times and centrifuged (Sorvall Rc 3C Plus, 3000 rpm) in order to get rid of the added acids and reach a pH fairly close to the pH of the raw clay. When Nc had been centrifuged it was distinctly divided into two phases; one reddish (Nc1) and one brownish one (Nc2). Due to their distinct different look, and therefore an assumed difference in chemical behavior, the phases were separated and treated individually during the rest of the study.

3.3.2 Removal of iron oxides

The centrifuged clays were dispersed in a citrate buffer (0.37 M sodium citrate dehydrate, 0.10 M sodium hydrogen carbonate and 1.20 M sodium chloride). By addition of sodium hydroxide pH was adjusted to 8.3. Sodium dithionite was then added (approximately 0.2 g $Na_2S_2O_4$/1 g of clay) and the suspensions were put on magnetic stirring for 70 hours. The slurries were finally washed four times with a solution of 0.5 M sodium chloride and 0.025 M hydrochloric acid and centrifuged (Sorvall Rc 3C Plus, 3000 rpm). The entire iron purification procedure was repeated once more.

3.3.3 Removal of organic matter

The clays were dispersed in 0.1 M acetic acid-sodium acetate buffer (5 ml/1 g clay), and 30 % w/w aqueous hydrogen peroxide (1.70 ml/1 g clay) was thereafter added. Drops of octyl alcohol were added so as to break the surface tension and impede the foam formation. The slurries were put on magnetic stirring for ten hours at a temperature of 90 °C. Distilled water was added when the slurries became too dry. The slurries were stirred for another 20 hours in room temperature and then washed three times with a 1 M sodium chloride solution and centrifuged. As the last step in the purification process, excess salt were removed by washing the clays with distilled water. During the centrifuging process, both Lcc and the Nc2 sample were divided into two fractions. It was no distinct boundary between them; still an attempt was done to separate the fractions so as to analyze them separately. A compilation of the final fractions are shown in Table 2. The centrifuged clays were dried at 50 °C in an oven for five days, ground into a fine powder and finally sifted.

Table 2. Two of the three soil samples were divided into different fractions during the purification procedure. The abbreviations of the distinguished fractions and the raw samples are listed below.

Namadzi clays (Nc)	Linthipe clays (Lcc)	Za mkt clays (Zmc)
Nc raw	Lcc raw	Zmc raw
Nc1	Lcc1	Zmc
Nc2	Lcc2	
Nc3		

3.4 Mineralogical analyses

Two different techniques were used in order to investigate the mineralogical composition of the clays; X-ray powder diffraction and scanning electron microscopy.

3.4.1 X-ray powder diffraction (XPD)

The purified soil was sifted and soil of the smallest fraction (f_1 < 0.032 mm) was packed into 1 mm glass capillary tubes and analyzed in a Bruker SMART CCD 1 K diffractometer with monochromatic MoKα (λ = 0.7093 Å) radiation. The obtained diffraction patterns were compared to a reference database (PDF-2) with the intention to identify crystalline phases. All purified samples were investigated and also one raw sample, Zmc raw, was randomly chosen.

3.4.2 Scanning electron microscopy (SEM)

A small amount of the sample (fraction f_2) was attached to a piece of carbon sticky tape and placed in the device, a Hitachi TM-1000 scanning electron microscope. The data received from the elementary analyses were interpreted by the software program SwiftED-TM. Both raw and purified materials were investigated.

3.5 Titrations

Acid and base titrations provide knowledge about the amphoteric properties of the surface groups of the clay mineral. The total concentration of acid-base active sites, $\{\equiv M\text{-}OH_{tot}\}$, was determined. Based on these data, the acidity constants ($K^s_{a1,app}$ and $K^s_{a2,app}$), the $pK^s_{a,intr}$ values as well as the pH_{pznpc} were calculated. Index intr stands for intrinsic, which means that they are extrapolated to zero net proton charge of the surface. Titrations were performed on all clay samples, both purified and raw, except for Zmc raw due to lack of material. When a sufficient amount of clay in fraction f_2 was available, this one was used. Otherwise, fraction f_3 was used.

3.5.1 Acid titration

2.0 g of clay was dispersed in 50.0 g of a 0.100 M sodium nitrate solution. 20.052 mM nitric acid was added stepwise from 0 to about 7 ml with an automatic burette (Metrohm 665 Dosimat) and pH was recorded at each equilibrium point using an Orion Ross electrode. The addition of acid was 0.20 ml in the beginning of the titration, but it was gradually increased in the end. The suspension was thoroughly stirred throughout the whole titration with a magnetic stirrer to maintain a stable suspension.

The measured pH value was plotted against the volume of added nitric acid in a titration curve, see Appendix 5. The beginning and the end of the graph were extrapolated. The value on the x-axis corresponding to the point where these regression lines cross each other is named V_e, the volume of surface sites. Since the concentration of the nitric acid was known, the amount of surface sites expressed in moles could be calculated. When dividing this value with the total volume, the total concentration of surface sites, $\{\equiv M\text{-}OH_{tot}\}$, was obtained for each point, see Eq. 2.

In order to determine the acidity constants, pK^s_a values for each measured point and pH_{pznpc}, the total concentration of surface charge, [*Q*], must be known. The only groups that give rise to surface charge in the studied system are $\equiv M\text{-}OH_2^+$ and $\equiv M\text{-}O^-$. The total concentration of surface charge is therefore expressed as follows:

$$[Q] = \{\equiv M\text{-}OH_2^+\} - \{\equiv M\text{-}O^-\} = c_A - c_B - [H_3O^+] + [OH^-], \qquad \text{Eq. 7}$$

where c_A and c_B stands for the amount of added acid and base respectively in molar. $[H_3O^+]$ and $[OH^-]$ are the free concentrations of hydronium ions/hydroxide ions that can be detected by the pH electrode.

$$c_A = \frac{c_{HNO_3} \cdot V_{added}}{V_{tot}} \qquad c_B = \frac{c_{NaOH} \cdot V_{added}}{V_{tot}} \qquad \text{Eq. 8a, b}$$

When titrating with an acid, it is assumed that no negative charges exist on the surface; hence $\{\equiv M\text{-}O^-\}$ can be neglected. This implies that: $[Q] = \{\equiv M\text{-}OH_2^+\} = c_A - [H_3O^+]$. Eq. 2 can therefore be rewritten as $\{\equiv M\text{-}OH_{tot}\} = [Q] + \{\equiv M\text{-}OH\}$ and replace $\{\equiv M\text{-}OH_2^+\}$ in Eq. 3b for the first acidity constant. This gives:

$$K^s_{a1,app} = \frac{(\{\equiv M\text{-}OH_{tot}\} - [Q]) \cdot [H_3O^+]}{[Q]}, \text{ where} \qquad \text{Eq. 9a}$$

$$pK^s_{a1,app} = -\log_{10} K^s_{a,app} \qquad \text{Eq. 9b}$$

The charge density, *Z,* was also calculated.

$$Z = \frac{[Q]}{\{\equiv M\text{-}OH_{tot}\}} \qquad \text{Eq. 10}$$

3.5.2 Base titration

A suspension of clay and sodium nitrate was prepared in the same manner as described in Chapter 3.5.1. However, the burette was now filled with 20.000 mM sodium hydroxide that was added stepwise.

It is assumed that there are no positively charged sites on the surface when titrating with a base; $\{\equiv M\text{-}OH_2^+\}$ can therefore be neglected.
This gives that $[Q] = \{\equiv M\text{-}O^-\} = -c_B + [OH^-]$. Thus, Eq. 2 can be rewritten as $\{\equiv M\text{-}OH_{tot}\} = \{\equiv M\text{-}OH\} + \{\equiv M\text{-}O^-\}$.

When $[Q]$ and $\{\equiv M\text{-}OH_{tot}\}$ are known, $K^s_{a2,app}$ can be calculated according to Eq. 11a, which is based on Eq. 4b. $[Q]$ is a negative number and must be multiplied with minus one in order to get a positive value of the stability constant.

$$K^s_{a2,app} = \frac{(-[Q])[H_3O^+]}{\{\equiv M\text{-}OH_{tot}\} - (-[Q])}, \text{ where} \qquad \text{Eq. 11a}$$

$$pK^s_{a2,app} = -\log_{10} K^s_{a2,app} \qquad \text{Eq. 11b}$$

The obtained $pK^s_{a,app}$ values from both acid and base titrations were plotted against the charge density, *Z*, in a diagram. By interpolating the two regression lines to $Z = 0$ with linear regression, $pK^s_{a1,intr}$ and $pK^s_{a2,intr}$ could be determined.

Finally, pH_{pznpc} was calculated according to the equation below:

$$pH_{pznpc} = \frac{pK^{s}_{a1,intr} + pK^{s}_{a2,intr}}{2} \qquad \text{Eq. 12}$$

3.6 Heavy metal adsorption

Due to lack of material, adsorption experiments were performed solely on five of the nine different soil samples, that is Zmc, Lcc1, Nc2, Nc raw and Lcc raw. When there was not enough material for experiments with all five chosen heavy metals, chromium(III), lead(II) and cadmium(II) were prioritized because of their importance in heavy metal pollution in Malawi.

3.6.1 Sample preparation

1.0 mM solutions of chromium(III), lead(II), cadmium(II), copper(II) and zinc(II) were prepared by solving a certain amount of metal salt in 0.1 M sodium nitrate solution.

Six centrifuge tubes were prepared for each soil and metal. To begin with, they all consisted of 0.5 g clay and 9 ml metal solution (i.e. simulated waste water). By addition of 0.1 M HNO_3 or 0.1 M NaOH, pH was adjusted to approximately 3, 4, 5, 6, 7 and 8, respectively, in the six tubes. See Appendix 2 for more detailed information regarding weighed in masses of soil, volumes of added acid and base and pH values. The samples were shaken for at least 48 hours and thereafter centrifuged at 3000 rpm for 30 minutes using a Kubota KS-5200C. The supernatant was decanted and its pH measured, see Appendix 3. In order to solve hydrolyze complexes in the solution phase, a drop of concentrated nitric acid was added before the samples were analyzed in Atomic absorption spectrometer (Perkin-Elmer AAnalyst 100 and 300).

3.6.2 Atomic absorption spectroscopy (AAS)

Atomic absorption spectroscopy (AAS) is a technique used to determine the concentration of a certain element in a sample. A Perkin-Elmer AAnalyst 100 instrument was used for analyses of copper(II), chromium(III) and cadmium(II) whereas a Perkin-Elmer AAnalyst 300 was used for lead(II) and zinc(II). The sample is split into separate atoms and the constituents are illuminated with light of a wavelength that is specific for the particular element (see Table 3). A higher content of the element causes a higher absorbance (Nationalencyklopedin, 2009f). If the obtained absorbance values are related to a calibration curve based on analyses of solutions with known metal concentrations, the concentration of metals remaining in the supernatant could be determined. It is thereafter possible to calculate the relative amount of adsorbed metal. Concentrations of metals in the supernatant are summarized in Appendix 3. More detailed information regarding the AAS technique can be found in Burrows *et al.* (2009).

Table 3. The wavelengths (λ) and slit widths (d_{sw}) shown in this table are chosen according to Analytical methods for atomic absorption spectrometry (1994).

	Cu^{2+}	Cr^{3+}	Pb^{2+}	Zn^{2+}	Cd^{2+}
λ/nm	327.4	357.9	283.3	213.9	228.8
d_{sw}/nm	0.7	0.7	0.7	0.7	0.7

3.7 Extended X-ray absorption fine structure (EXAFS)

EXAFS makes it possible to determine how metals are bound to surfaces in a soil sample. One metal, chromium(III), was chosen and its adsorption to Zmc raw and Zmc was studied.

3.7.1 Sample preparation

0.5 g of clay (Zmc raw and Zmc respectively) was suspended in 5 mM chromium(III) solution, which was prepared by dissolving $Cr(NO_3)_3 \cdot 9H_2O$ in distilled water. The pH values of the suspensions were adjusted to pH ≈ 6 by addition of sodium hydroxide. The samples were shaken for 48 hours and thereafter centrifuged at 3000 rpm for 30 minutes using a Kubota KS-5200C. The supernatant was decanted and the clay left to dry at room temperature.

3.7.2 Analyses

Measurements were performed at MAX-lab, Lund University. More information about the technique and procedure can be found on the homepage of MAX-lab.

4 Results and discussion

The mineral content of the clays has been examined and the chemical properties of the clays and their ability to adsorb heavy metals have been investigated. Useful information about the three natural clays has been obtained through the laboratory experiments carried out in the study. The results from the mineralogical analyses, acid and base titrations, adsorption experiments and the EXAFS analyses are presented and discussed here.

4.1 Mineralogical analyses

The diffraction patterns from the analyses with the X-ray powder diffractometer prove that the studied material is at least partly crystalline. Still, the broad peaks (see Figs. 8 and 9) show that the crystallinity is low, and that some of the material doubtless is amorphous. When comparing the patterns with reference patterns in the PDF-2 database it is evident that all the samples consist of some type of quartz (ICDD, 2009). Three samples seem to be composed of hexagonal quartz, another three of tetragonal quartz and the last one seems to be a mixture of these two. Identification of additional phases is difficult due to the broad peaks. Yet, there is an indication that one sample, Zmc, contains of the iron oxide hematite, but the quality of the XRD-patterns are not sufficiently good to verify this.

As the weathering process proceeds, the mineral composition of a soil shifts from clay mineral of 2:1 type, e.g. illite, vermiculite and smectite, and primary minerals to an increased content of kaolinite mineral and iron and aluminum oxides and hydroxides (Eriksson *et al.*, 2005). Presence of hematite thus indicates that the weathering is extended, which is reasonable because of the warm climate and periods of high precipitation in Malawi.

Despite the fact that it is not possible to identify any further phases than quartz from the XRD analyses, the energy dispersive spectrometer (EDS) analyses confirms that additional elements are present, see Appendix 4. X-ray powder diffraction is a phase identification method where only crystalline phases can be detected whereas EDS can identify the elements in both crystalline and amorphous material. Elements confirmed to be present by EDS, but not detected by XRD, are consequently amorphous. A disadvantage of EDS is that oxygen is not directly measurable. It is therefore not possible to make an absolute determination of the elements relative apportionment and in that manner identify possible minerals.

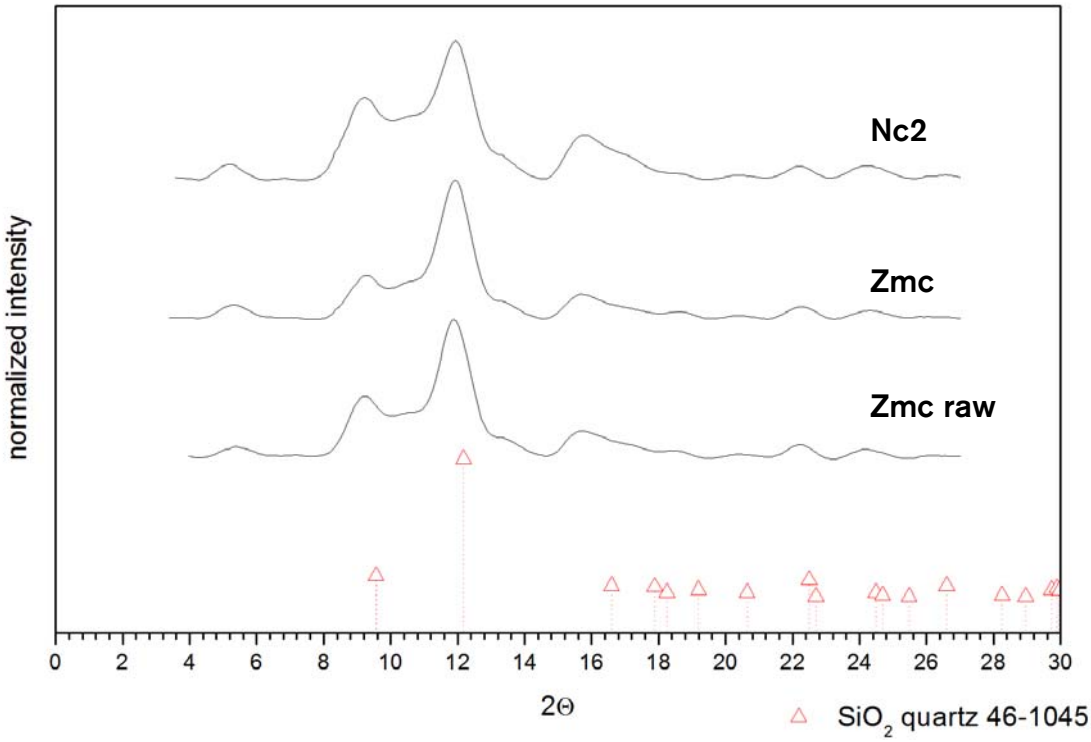


Figure 8. X-ray powder diffraction pattern. The reference pattern of hexagonal quartz is marked with red triangles.

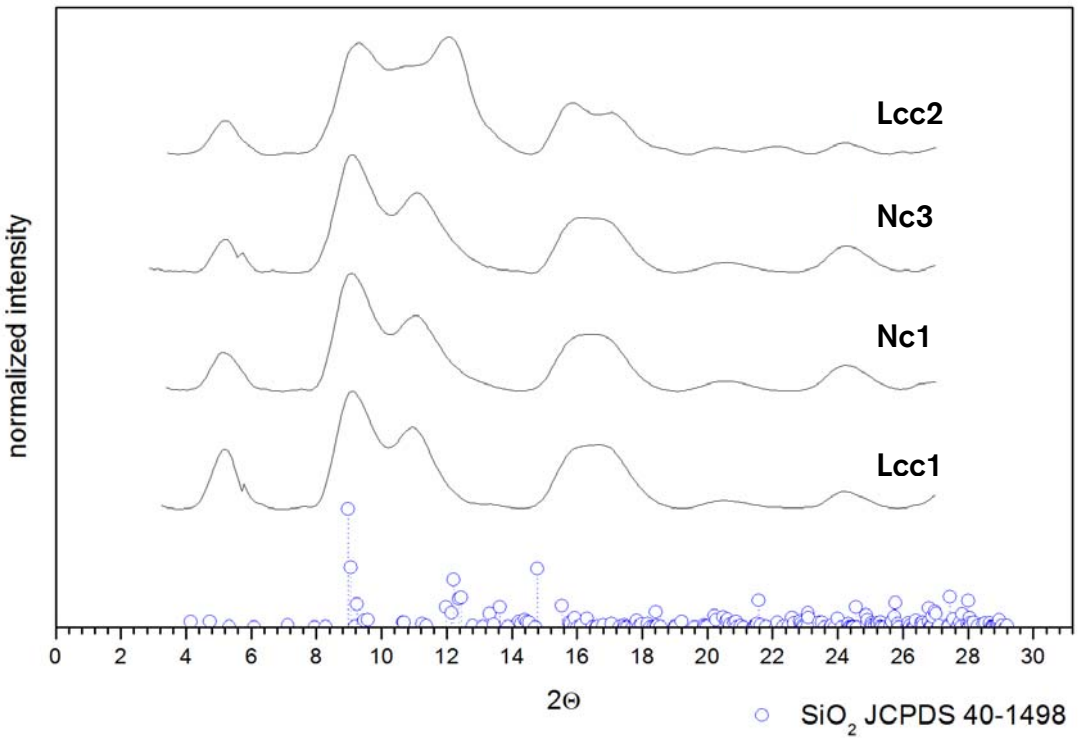


Figure 9. X-ray powder diffraction pattern. The reference pattern of tetragonal quartz is marked with blue circles.

The enlarged images produced by SEM show that the studied material is not uniform, see Figs. 10-12. There are loads of tiny particles as well as particles of a somewhat larger size. The images also show presence of particles of a form that very much indicates that they are crystalline. Their cleavage surfaces are sharp and clean.

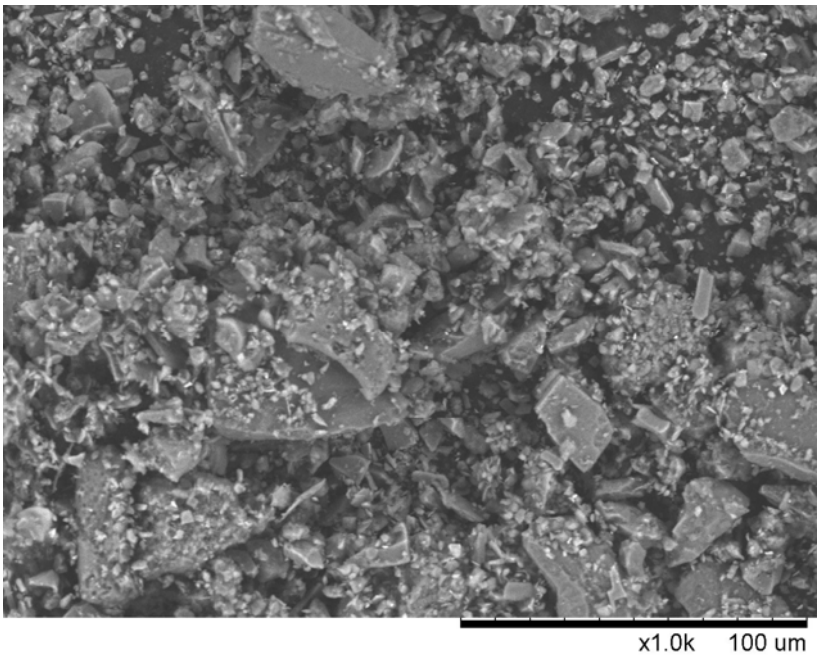


Figure 10. SEM image of Nc2 at 1000 times magnification.

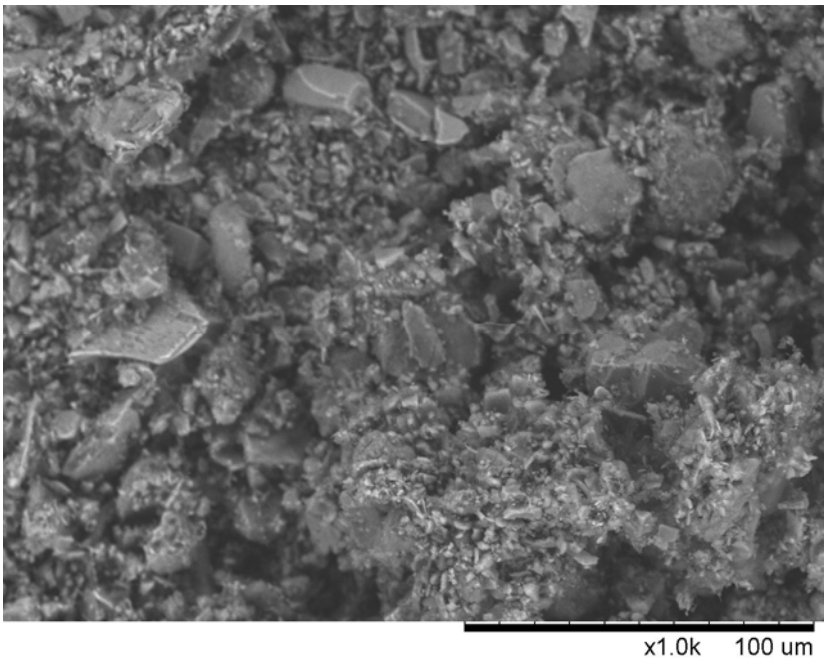


Figure 11. SEM image of Lcc2 at 1000 times magnification.

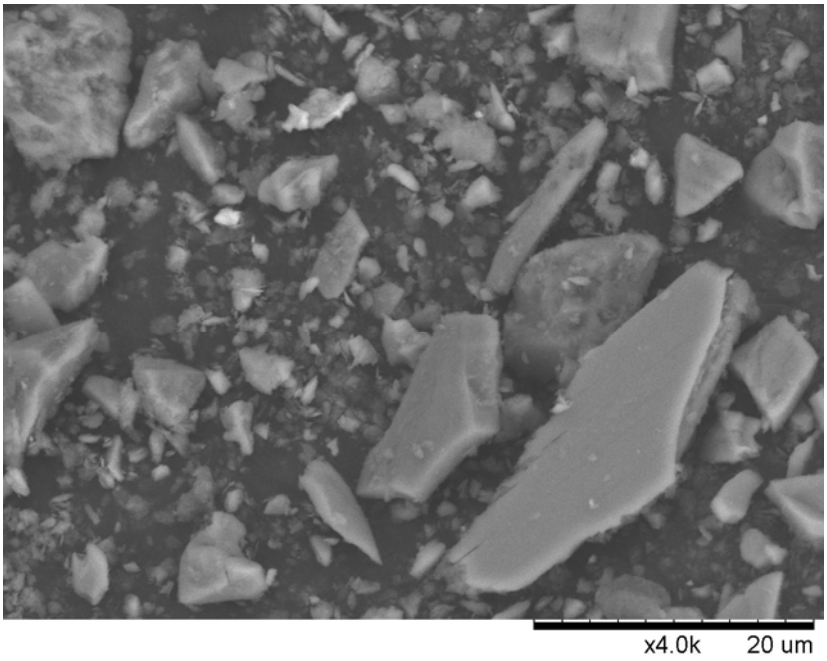


Figure 12. SEM image of Zmc at 4000 times magnification.

4.2 Acid-base properties of the clays

The determination of the acidity constants was based on the total concentration of surface sites, $\{\equiv M\text{-}OH_{tot}\}$, which in turn was calculated from the volume of surface sites, V_e, obtained from the acid titration. This resulted in graphs where the pK_a values increased with increased positively charged surface and decreased with a more negatively charged surface. This erroneous relation implies that the method used for studies of pure phases is not applicable for the mixed clays studied in this thesis. Therefore, the graphs were adjusted to agree with the correct form of the function, by multiplying $\{\equiv M\text{-}OH_{tot}\}$ by a suitable factor, X_{corr}. Regardless of which X_{corr} that was used for Lcc raw and Nc raw, their pK_a values still increased with increasing positive charge and decreased with increasing negative charge. This is assumed to be caused by the organic matter, which has acid-base properties that can influence and thus disturb the system. What kind of specific mechanisms that give rise to this behavior is unclear but it is obvious that organic matter and its functional groups (primarily carboxylic but also phenolic OH, alcoholic OH and amino groups) compete with the mineral surface for the hydrogen ions.

Fig. 13 illustrates how pK_a vary with charge density, Z, for Zmc. Graphs for the other soils can be found in Appendix 6. The pH_{pznpc} values, which are obtained by dividing the sum of the intrinsic pK_a value for the first and second dissociation step with a factor two, are compiled in Table 4. It is important to keep in mind though, that these values are mean values for the numerous of different minerals that are presumed to exist in each soil sample.

Table 4. pH_{pznpc} values for the different soils.

sample	Zmc	Nc raw	Nc1	Nc2	Nc3	Lcc raw	Lcc1	Lcc2
pH_{pznpc}	6.45	8.58	5.73	5.94	5.85	9.00	5.76	5.90

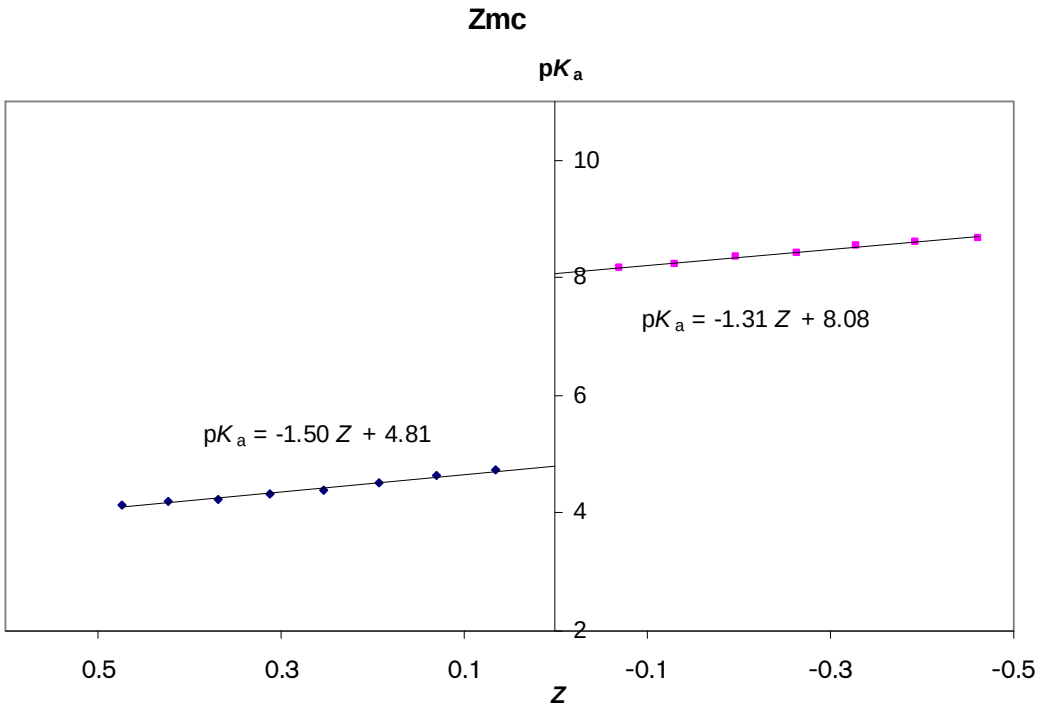


Figure 13. The negative logarithmic form of the acidity constant, pK_a, plotted against charge density, Z, for Zmc. p$K^s_{a1,intr}$ = 4.81, p$K^s_{a2,intr}$ = 8.08, pH_{pznpc} = 6.45.

From Table 4, it is evident that the different purified fractions within the same soil type behave chemically exactly the same. Their pH_{pznpc} values are within the estimated errors equal. They are 5.76 and 5.90 for Lcc and vary from 5.73 to 5.94 for Nc. In spite the fact that the fractions furthermore were coloured differently, this implies that their mineral composition are more or less identical. The color of a soil is a function of light scattering, the form and size of the particles and does not depend on the mineral composition.

The pH_{pznpc} values for the Lcc and Nc samples were quite equivalent whereas Zmc had a somewhat higher value, which indicates that its mineral composition is different from the other two. Even though this is a reasonable conclusion, it was difficult to find clear evidence for it from the EDS results. Nevertheless, from the EDS analyses some general conclusions about the mineral composition of the three soils can be drawn. One of them is that the iron content in many samples is far too high (see e.g. Fig. A4a in Appendix 4) to be explained solely by isomorphic substitution of iron for aluminum in the octahedral sheets. Iron oxides or hydroxides must therefore be present in the soils. In Nc1 the weight percent of silicon and aluminum was rather equal (Fig. A4b). Since their atomic weights are similar, roughly the same amounts of silicon and aluminum atoms exist in the sample. This might imply that the sample consists of 1:1 layer mineral, e.g. kaolinite whose chemical formula can be found in Table 5. The experimentally obtained pH_{pznpc} for Nc1 is however higher than the reference value; 5.73 compared to 4.6. In the remaining samples, the silicon content exceeds the aluminum content, which could indicate presence of 2:1 layer mineral. Illite is an example of this kind of mineral. Anyhow, it is obvious that the purified samples not only consist of quartz, since quartz has a pH_{pznpc} value that is many pH units lower than those observed for the purified samples.

Table 5. pH_{pznpc} values for different minerals.

mineral	chemical formula	pH_{pznpc}	basic information
quartz	SiO_2	2.0	primary mineral, framework silicate
kaolinite	$Al_2Si_2O_5(OH)_4$	4.6	secondary mineral, 1:1 layer silicate
illite	$M_x[Si_{6.8}Al_{1.2}]Al_3Fe_{0.25}Mg_{0.75}O_{20}(OH)_4$	-	secondary mineral, 2:1 layer silicate
hematite	α–Fe_2O_3	8.5	secondary mineral, oxide
goethite	α-FeOOH	7.8	secondary mineral, oxide
alumina	α–Al_2O_3	9.1	secondary mineral, oxide
gibbsite	α-$Al(OH)_3$	5.0	secondary mineral, hydroxide

Source: Stumm, 1992. M denotes exchangeable cations of varying charge that are not a part of the mineral structure.

Higher pH_{pznpc} values were obtained for raw than purified material. This is likely to be caused by presence of iron and maybe also aluminum oxides in the raw samples, which are assumed to exist according to SEM and XRD analyses. These oxides have high pH_{pznpc} values, e.g. pH_{pznpc} = 8.5 for hematite (Stumm, 1992), see Table 5. This agree relatively well with that of the raw samples; pH_{pznpc} = 8.58 for Nc raw and pH_{pznpc} = 9.00 for Lcc raw.

4.3 Adsorption

All the soil samples show the same adsorption pattern; chromium(III) is most effectively removed from the aqueous phase, thereafter comes lead(II), copper(II), zinc(II) and cadmium(II), see Figs. 14-18. Chromium(III), lead(II) and copper(II) are in principle completely removed from the aqueous phase at approximately pH = 7. For the two first ones, the adsorption is very high already at lower pH values. At pH = 7.56, which is the last measured point for Zmc, zinc(II) is adsorbed to 75 %. The removal of cadmium(II) is not complete in any of the purified samples. It reaches 77 % at the last measure point at pH = 7.49 for Lcc1, whereas it just get to 50 % at pH = 7.60 for Zmc.

The investigated metals are adsorbed to a higher extent in raw than purified clay. This is most evident for cadmium(II), which removal increases considerably and exceeds 90 % in Nc raw and Lcc raw. The predominant functional groups of soil organic matter are carboxylic groups, which dissociate in the interval 3 < pH < 6, and will consequently be negatively charged at higher pH values. There will not be a competition between the hydrogen ions and the metal ions, and the latter ones can therefore easily be adsorbed to the organic matter. Other functional groups on organic matter are hydroxyphenol and amino groups, but their pK_a values are considerable higher, > 9 and 9-11 respectively (McBride, 1994). In addition, the metals can bind to iron oxides in the raw samples. Their pH_{pznpc} are however high, but inner-sphere complexes can be formed even when the net charge of the surface is positive, e.g. pH < pH_{pzc}. Thus, there is no point in purifying the clays that will be utilized for heavy metal removal since organic matter and iron oxides have a positive influence on the adsorption.

The pH values of the studied soils are high, see Table 6. The alkaline properties of the soils are most likely to promote hydrolyses of chromium(III) and lead(II). Hydrolysis of these two cations is facilitated due to the high charge density of chromium and the electron configuration of lead (Chang, 2005). Other alkaline clays from Malawi have by EXAFS studies been confirmed to promote hydrolyses of heavy metals (Sajidu, 2008). EXAFS analyses performed in this study prove that chromium(III) undergoes hydrolysis, and CrOOH is pointed out as a possible product. However, the results showed that the extent of hydrolysis was not that high and additional mechanism must be involved in the

removal of chromium(III). Inner-sphere complexes are likely to be formed. Inner-sphere complexes are also assumed to account for the removal of chromium(III) taking place at low pH values, since hydrolysis of chromium(III) occurs not until pH > 3. Furthermore, hydrolysis of chromium(III) was lower in Zmc raw than in Zmc. Presence of organic matter increases the formation of surface complex and impedes hydrolysis.

Table 6. Natural pH values of the different soil samples.

sample	Nc raw	Nc1	Nc2	Nc3	Lcc raw	Lcc1	Lcc2	Zmc raw	Zmc
pH	8.59	5.70	5.97	5.79	9.08	5.81	5.86	-	6.53

When a metal complex undergoes hydrolysis, its hydrogen ions are removed stepwise. An example of a simple chromium(III) hydrolysis is shown in Eq. 13-15. Finally, a solid uncharged complex is formed. It will precipitate and be attached to a surface and the metal will therefore be removed from the aqueous phase.

$$Cr(H_2O)_6^{3+} + H_2O \rightleftharpoons CrOH(H_2O)_5^{2+} + H_3O^+ \qquad \text{Eq. 13}$$

$$CrOH(H_2O)_5^{2+} + H_2O \rightleftharpoons Cr(OH)_2(H_2O)_4^{+} + H_3O^+ \qquad \text{Eq. 14}$$

$$Cr(OH)_2(H_2O)_4^{+} + H_2O \rightleftharpoons Cr(OH)_3\,(s) + H_3O^+ + 3H_2O \qquad \text{Eq. 15}$$

As long as the chromium complex is charged, it is soluble in water. However, the process is irreversible as soon as the solid phase is formed due to slow kinetics.

Copper(II), zinc(II) and cadmium(II) are on the other hand less likely to undergo hydrolysis. These metals are probably removed from the aqueous phase through formation of surface complexes. The adsorption starts at pH values below pH_{pznpc}, which indicates formation of inner-sphere complexes. Although, this does not automatically mean that there are no outer-sphere complexes. Eq. 16 describes the inner-sphere surface complexation of cadmium(II), which in principle is regarded as an irreversible process whereas ions adsorbed through outer-sphere complexes are readily exchangeable (Eq. 17).

$$\equiv M\text{-}OH + Cd^{2+} + H_2O \rightleftharpoons \equiv M\text{-}O\text{-}Cd^{+} + H_3O^+ \qquad \text{Eq. 16}$$

$$\equiv M\text{-}O^- + Cd^{2+}\,(aq) \rightleftharpoons \equiv M\text{-}O^{-}\cdots Cd^{2+}\,(aq) \qquad \text{Eq. 17}$$

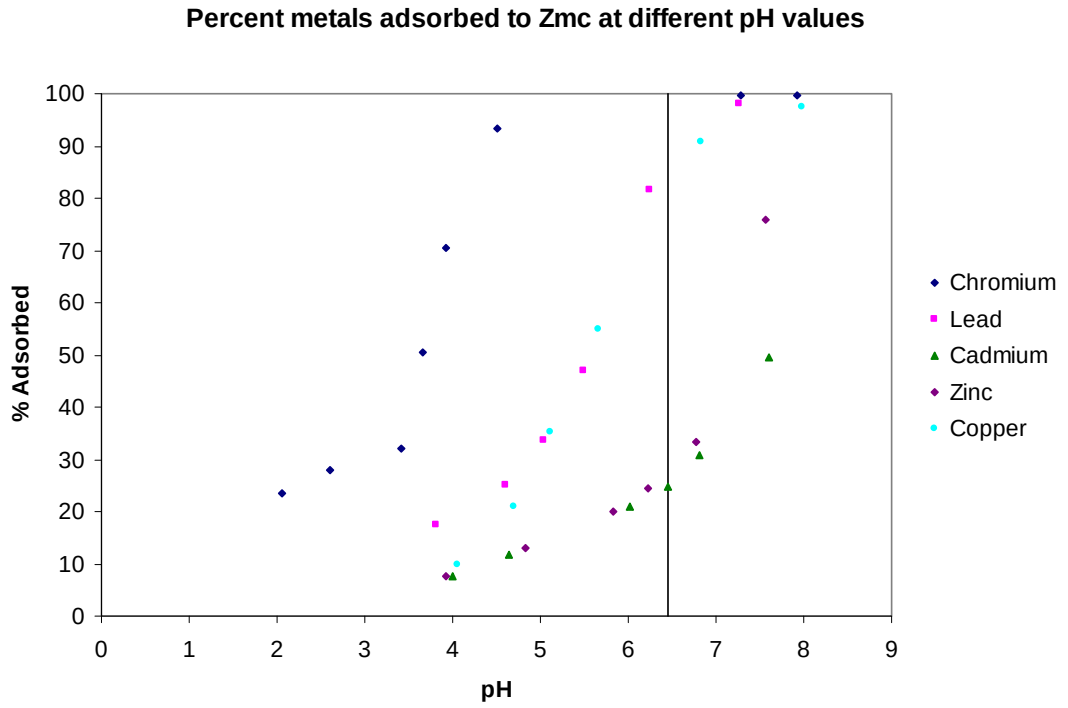


Figure 14. Percent chromium(III), lead(II), cadmium(II), zinc(II) and copper(II) adsorbed to Zmc at different pH values. pH_{pznpc} = 6.45 as marked by the vertical line.

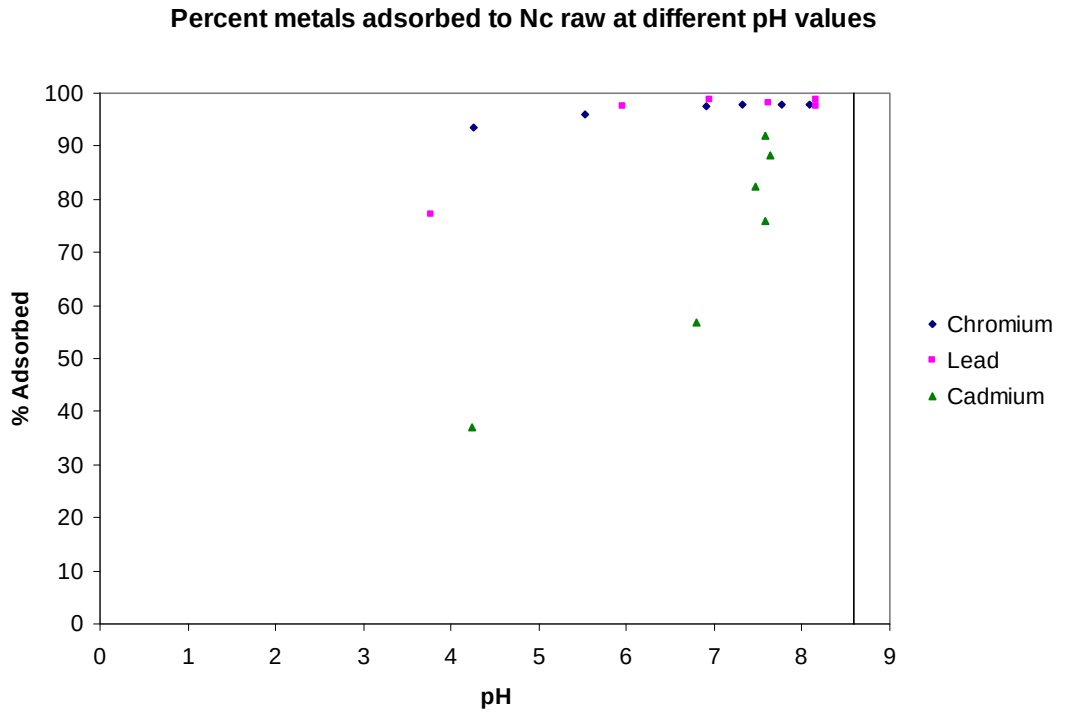


Figure 15. Percent chromium(III), lead(II) and cadmium(II) adsorbed to Nc raw at different pH values. pH_{pznpc} = 8.58 as marked by the vertical line.

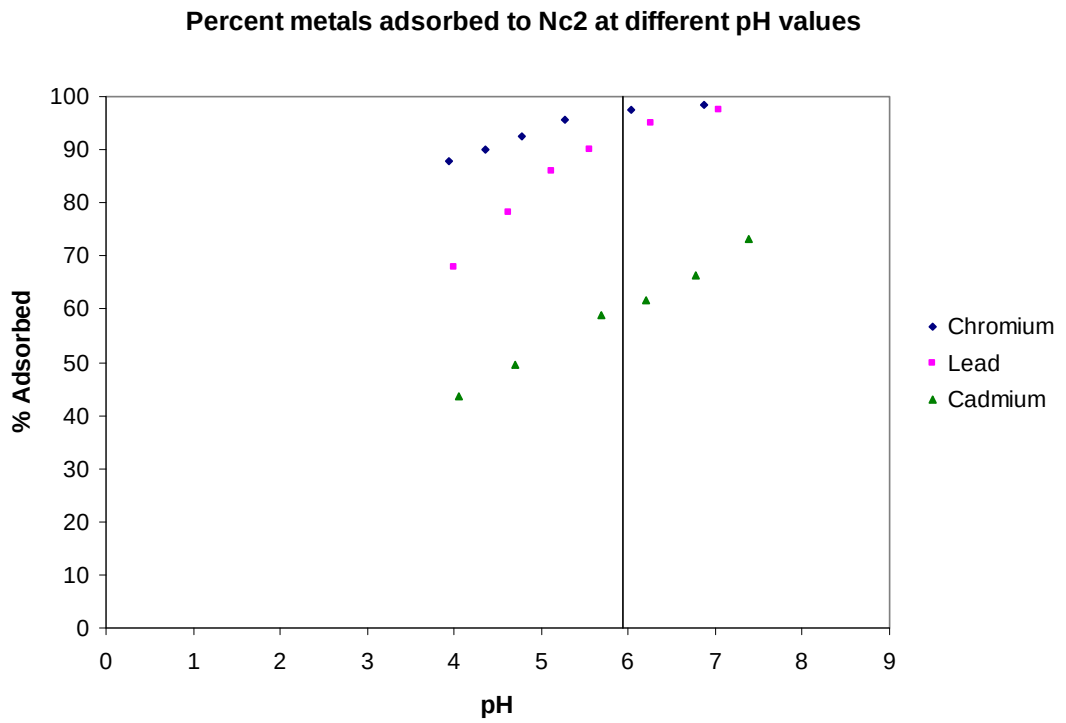


Figure 16. Percent chromium(III), lead(II) and cadmium(II) adsorbed to Nc2 at different pH values. pH_{pznpc} = 5.94 as marked by the vertical line.

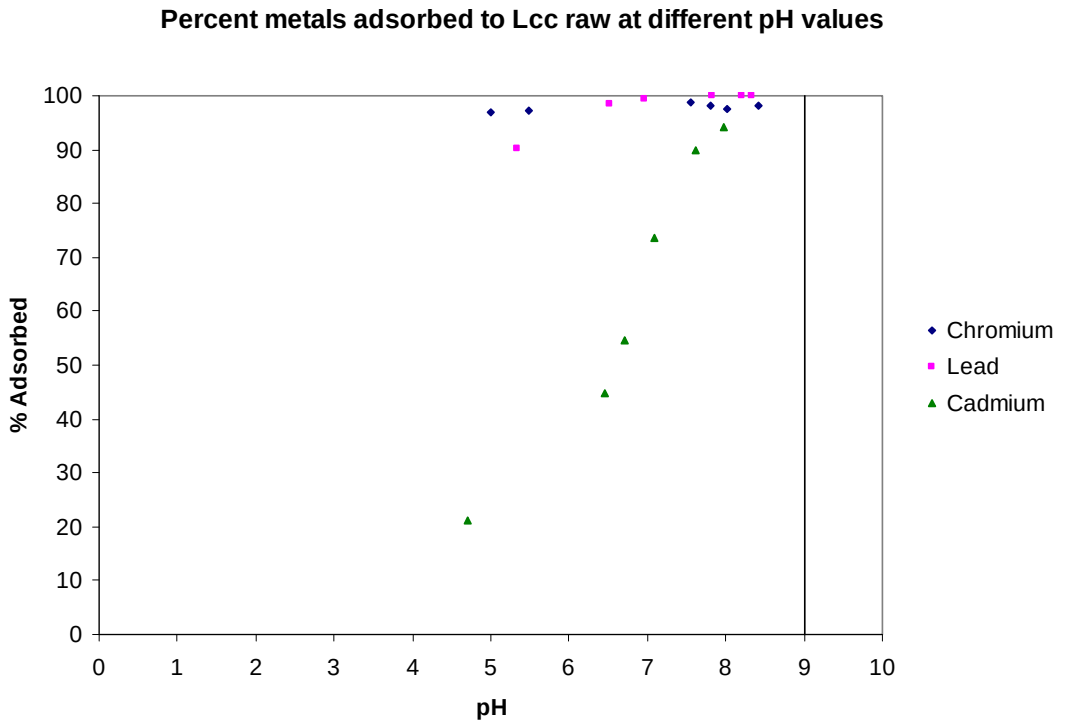


Figure 17. Percent chromium(III), lead(II) and cadmium(II) adsorbed to Lcc raw at different pH values. pH_{pznpc} = 9.00 as marked by the vertical line.

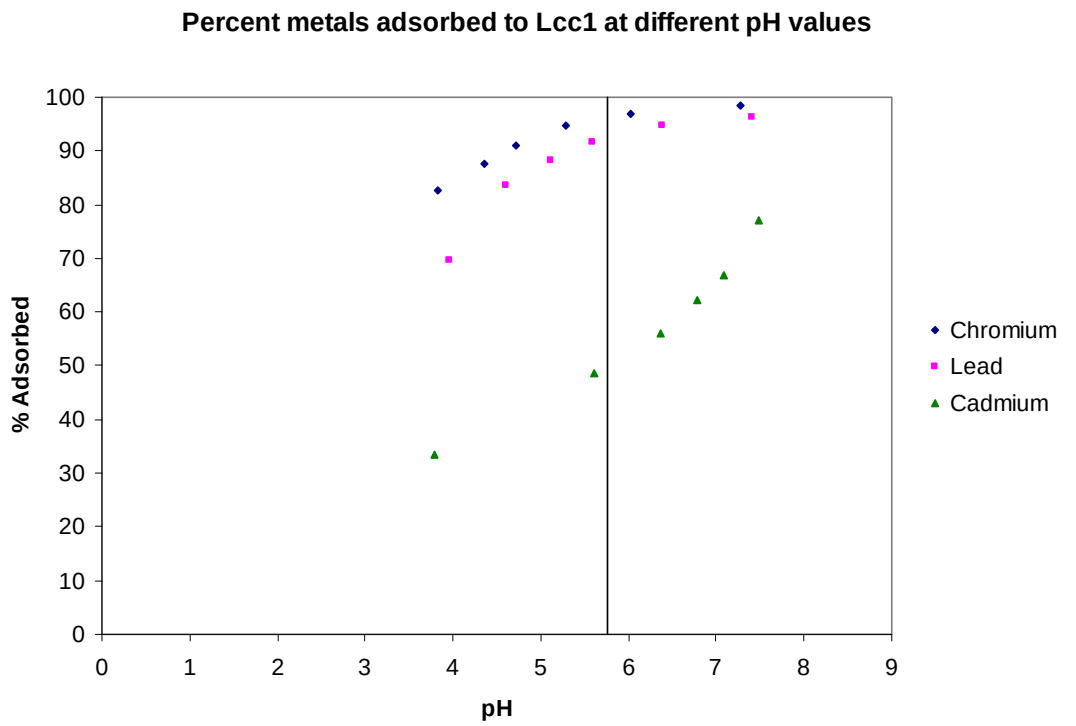


Figure 18. Percent chromium(III), lead(II) and cadmium(II) adsorbed to Lcc1 at different pH values. pH_{pznpc} = 5.76 as marked by the vertical line.

One of the cadmium(II) standard solutions was by mistake not acidified before measurements in the atomic absorption spectrometer. However, cadmium(II) does not hydrolyse with water to any larger extent. Cadmium hydroxides are consequently not formed and the solution consists of free Cd^{2+} ions. For that reason, this source of error should not have influenced the results that much.

The metal concentrations used in this study are incomparably higher than those observed in streams in Malawi. High concentrations generate a more pronounced description of the adsorption and facilitate the drawing of conclusions. Even though adsorption is assumed to increase with increased metal concentration, the method will most likely have good potential in reality as well, due to its high efficiency in this study. Chromium(III), lead(II) and copper(II) will probably be successfully removed from the aqueous phase whereas the efficiency presumably is lower for zinc(II) and cadmium(II).

Zmc has originated an exemplary pK_a versus Z plot as well as nicely formed adsorption curves (see Figs. 13 and 14). It is therefore likely that this soil has a more uniform composition than the other two studied soils. A mixture of several minerals with different properties are assumed to create a less distinct and consistent picture.

Studies of natural mixed clays are crucial since they describe the reality. Investigations of single phase systems can also be of great importance but these kinds of systems do not exist in nature. Furthermore, a mixture of two materials does not necessarily behave like a mean value of its two components, since they might affect each other in an unpredictable way.

4.4 Future perspectives

This study has proven that the investigated clays have good potential to act as adsorbents for removal of the five studied heavy metals. This indicates that natural mixed clays can be used for this purpose but each soil is unique and no general conclusions can be drawn based on just a few studies. However, this study and previous studies have shown that natural mixed clays actually are very interesting and further investigations should be performed in order to verify this. Research regarding practical solutions is also needed so as to develop a method that is applicable at a small-scale level.

5 Conclusions

All investigated soil samples contain fractions of crystalline quartz and amorphous iron and aluminum oxides/hydroxides. There is also an indication for existence of crystalline hematite. The clay mineral fraction in the samples seems to mainly consist of amorphous material, since no indications were observed in the X-ray powder diffractograms.

Laboratory experiments showed that the raw samples had higher pH_{pznpc} values than the purified ones. This may be explained by the content of iron and possibly aluminum oxides/hydroxides in the non-treated samples.

In the purified soil samples, chromium(III), lead(II) and copper(II) were completely removed from the aqueous phase at pH ≈ 7, whereas zinc(II) and cadmium(II) were not fully adsorbed at the investigated pH interval. However, all studied heavy metals were essentially fully removed from the aqueous phase of the raw material at pH values above pH_{pznpc}. Thus, there is no reason to purify the soil, since untreated soils are effective in a wider pH range.

The alkaline properties of the clays promote hydrolysis of both chromium(III) and lead(II) that precipitate and therefore may get sorbed on the surface. Copper(II), zinc(II) and cadmium(II) probably form surface complexes, mainly inner-sphere ones.

6 Acknowledgements

Many thanks go to Ingmar for superb supervision and to Daniel that have taken the time to answer all my questions. I really appreciate it and it has been a pleasure having you as my assistant supervisor. Ingmar, I am fortunate and grateful to have had you as supervisor! I would also like to thank everyone that has helped me with my laboratory work, especially Gulaim, Robert, Kai and Bernt!

7 References

ALS Laboratory Group-Analytical chemistry & testing services. Homepage: http://www.alsglobal.se. Accessed: 2009-05-23.

Analytical methods for atomic absorption spectroscopy (1994), The Perkin-Elmer Corporation, USA.

Atkins, P.W. (1996) *The elements of physical chemistry 2nd Ed.*, Oxford University Press, Oxford, UK.

Bhattacharya, A.K., Mandal, S.N. and Das, S.K. (2006) Adsorption of Zn(II) from aqueous solution by using different adsorbents, *Chemical Engineering Journal*, **123**, 43-51.

Bhattacharyya, K.G. and Gupta, S.S. (2008), Kaolinite and montmorillonite as adsorbents for Fe(III), Co(II) and Ni(II) in aqueous medium, *Applied Clay Science*, **41**, 1-9.

Burrows, A., Holman, J., Parsons, A., Pilling, G., and Price, G. (2009) *Chemistry: introducing inorganic, organic and physical chemistry*, Oxford University Press, New York, USA.

Chang, R. (2005) *Chemistry 8th Ed.*, McGraw-Hill, New York, USA.

Duffus, J.H. (2002) "Heavy metals" – a meaningless term? *Pure and Applied Chemistry*, **74**(5), 793-807.

Eren, E. (2008) Removal of copper ions by modified Unye clay, Turkey, *Journal of Hazardous Materials*, **159**, 235-244.

Eriksson, J., Nilsson, I. and Simonsson, M. (2005) *Wiklanders marklära,* Studentlitteratur, Lund, Sweden.

International Centre for Diffraction Data (ICDD), Powder Diffraction File (PDF-2; 2008 release). Homepage: http://www.icdd.com/products/pdf2.htm. Accessed: 2009-06-08.

Jalilehvand, F. (2000) *Structure of hydrated ions and cyano complexes by X-ray absorption spectroscopy*, Doctoral dissertation, Royal Institute of Technology, Stockholm, Sweden.

MAX-lab. Homepage: http://www.maxlab.lu.se. Accessed: 2009-05-29.

McBride, M.B. (1994) *Environmental chemistry of soils,* Oxford University Press, New York, USA.

Mora, A., Mac-Quhae, C., Calzadilla, M. and Sánchez, L. (2009) Survey of trace metals in drinking water supplied to rural populations in the eastern Llanos of Venezuela, *Journal of Environmental Management*, **90**, 752-759.

Nationalencyklopedin online.
2009a Accessed: 2009-02-18 Entry: *Malawi*
2009b Accessed: 2009-05-09 Entry: *tungmetall*
2009c Accessed: 2009-05-09 Entry: *kadmium*
2009d Accessed: 2009-05-09 Entry: *krom; zink; koppar*
2009e Accessed: 2009-01-20 Entry: *elektronmikroskop*
2009f Accessed: 2009-04-27 Entry: *atomabsorptionsspektrometri*
2009g Accessed: 2009-05-22 Entry: *kristallografi*

Sajidu, S.M.I. (2008) *Characterisation and interaction of mixed alkaline clays and moringa seeds with heavy metals in contaminated water*, Doctoral dissertation, University of Malawi, Zomba, Malawi.

Sposito, G. (1989) *The chemistry of soils*, Oxford University Press, New York, USA.

Stumm, W. (1992) *Chemistry of the solid-water interface: processes at the mineral-water and particle-water interface in natural systems,* John Wiley & Sons Inc, New York, USA.

Sällström, M. (2008) *Physico-chemical characteristics of some soils from Mali and their potential in heavy metal removal*, Master's thesis, Swedish University of Agricultural Sciences, Uppsala, Sweden.

Wikipedia
2009a Accessed: 2009-05-18 Entry: *Malawi* (Swedish written version)
2009b Accessed: 2009-05-15 Entry: *Malawi* (English written version)

WHO (2006) *Guidelines for drinking water quality 3rd Ed.*

Appendix 1: Purification process

Table A1a. Removal of carbonates from clay samples through addition of sodium acetate-acetic acid buffer. Weighed in sample masses (m_{clay}), volume of added sodium acetate-acetic acid buffer (V_{sb}) and its concentration (c_{sb}).

sample	m_{clay}/g	V_{sb}/ml	c_{sb}/M
Nc	100.000	250	0.40
Lcc	100.000	225	0.44
Zmc	80.001	125	0.64

Table A1b. Removal of iron oxides from clay samples by addition of citrate buffer and sodium dithionite. Weighed in sample masses (m_{clay}), volume of added citrate buffer (V_{cb}) and mass of sodium dithionite ($m_{Na_2S_2O_4}$).

sample	m_{clay}/g	V_{cb}/ml	$m_{Na_2S_2O_4}$/g	
			1st purification	2nd purification
Nc1	39.657	107.1	7.929	7.921
Nc2	60.343	162.9	12.074	12.076
Lcc	100.000	270.0	20.030	20.032
Zmc	80.001	216.0	15.990	16.000

Table A1c. Removal of organic matter by addition of acetic acid-sodium acetate buffer and hydrogen peroxide. Weighed in sample masses (m_{clay}), volume of added 0.1 M acetic acid-sodium acetate buffer (V_{ab}) and 30 % w/w aqueous hydrogen peroxide ($V_{H_2O_2}$).

sample	m_{clay}/g	V_{ab}/ml	$V_{H_2O_2}$/ml
Nc1	39.657	198.3	67.4
Nc2	60.343	301.7	102.6
Lcc	100.000	500.0	170.0
Zmc	80.001	400.0	136.0

Appendix 2: Adsorption data 1

Table A2a. Metal solutions used in adsorption experiment. Concentration of metal solutions (*c*).

	Cu^{2+}	Cr^{3+}	Pb^{2+}	Zn^{2+}	Cd^{2+}
salt	$Cu(NO_3)_2 \cdot 3H_2O$	$CrN_3O_9 \cdot 9H_2O$	$Pb(NO_3)_2$	$Zn(NO_3)_2 \cdot 4H_2O$	$Cd(NO_3)_2 \cdot 4H_2O$
c/g/l	0.242	0.400	0.330	0.262	0.310
c/mM	1.00	1.00	0.99	1.00	1.00

Table A2b. Preparation of samples for adsorption experiments on Zmc. Soil fraction f_3 is used for Pb, Zn and Cr. Soil fraction f_2 is used for Cu and Cd. Masses of clay (*m*), pH and volume of added acid (V_{acid}) and base (V_{base}).

	Sample	Cu	Cr	Pb	Zn	Cd
m/g	1	0.502	0.501	0.502	0.502	0.502
	2	0.501	0.501	0.501	0.501	0.502
	3	0.502	0.501	0.502	0.502	0.500
	4	0.502	0.501	0.500	0.502	0.501
	5	0.500	0.500	0.504	0.502	0.501
	6	0.501	0.502	0.503	0.503	0.500
	7		0.502			
	8		0.502			
pH	1	3.04	3.03	3.09	3.01	3.03
	2	4.00	3.98	4.05	3.94	3.98
	3	5.02	5.02	4.98	4.94	4.97
	4	5.97	5.94	5.95	5.99	6.02
	5	7.00	7.05	6.94	6.92	7.04
	6	8.02	8.05	7.94	7.94	7.95
	7		2.42			
	8		1.97			
V_{acid}/µl	1	133.84	99.14	107.07	114.01	158.62
	2	44.61		27.76	39.66	69.40
	3				14.87	19.83
	4					
	5		4.96			4.96
	6	4.96				
	7		237.94			
	8		589.88			
V_{base}/µl	1					
	2					
	3		74.36			
	4	59.48	148.71	29.74	1.98	
	5	148.71	232.98	99.14	32.72	34.70
	6	228.02	297.42	158.62	124.92	99.14
	7					
	8					

Table A2c. Preparation of samples for adsorption experiments on Lcc1. Soil fraction f_4. Masses of clay (m), pH and volume of added acid (V_{acid}) and base (V_{base}).

	Sample	Cr	Pb	Cd
m/g	1	0.500	0.500	0.502
	2	0.501	0.502	0.500
	3	0.501	0.502	0.500
	4	0.501	0.501	0.501
	5	0.501	0.502	0.500
	6	0.501	0.501	0.500
pH	1	2.99	3.06	3.02
	2	3.95	4.01	3.97
	3	4.96	5.04	4.96
	4	5.99	6.00	6.05
	5	6.96	7.01	6.99
	6	7.99	8.01	8.01
V_{acid}/µl	1	237.94	297.42	386.65
	2	49.57	99.14	158.62
	3		4.96	49.57
	4	4.96		
	5			
	6			
V_{base}/µl	1			
	2			
	3	54.53		4.96
	4	153.67	64.44	19.83
	5	221.08	158.62	69.40
	6	356.90	257.76	223.07

Table A2d. Preparation of samples for adsorption experiments on Nc2. Soil fraction f_1. Masses of clay (m), pH and volume of added acid (V_{acid}) and base (V_{base}).

	Sample	Cr	Pb	Cd
m/g	1	0.501	0.500	0.501
	2	0.501	0.502	0.500
	3	0.502	0.500	0.500
	4	0.502	0.500	0.501
	5	0.500	0.500	0.502
	6	0.501	0.501	0.501
pH	1	3.07	3.07	3.05
	2	3.98	4.00	4.05
	3	5.02	5.05	5.06
	4	6.03	6.03	5.98
	5	7.03	7.04	7.00
	6	7.98	8.00	7.99
V_{acid}/μl	1	149.70	250.52	297.42
	2	29.74	79.31	148.71
	3		4.96	44.61
	4	7.93		14.87
	5			
	6			
V_{base}/μl	1			
	2			19.83
	3	66.42		4.96
	4	153.67	49.57	4.96
	5	198.28	128.88	34.70
	6	262.72	198.28	114.01

Table A2e. Preparation of samples for adsorption experiments on Nc raw. Soil fraction f_4. Masses of clay (m), pH and volume of added acid (V_{acid}) and base (V_{base}).

	Sample	Cr	Pb	Cd
m/g	1	0.500	0.501	0.500
	2	0.501	0.501	0.502
	3	0.502	0.501	0.502
	4	0.501	0.502	0.501
	5	0.502	0.500	0.502
	6	0.500	0.501	0.502
pH	1	2.97	2.93	3.00
	2	3.95	4.00	4.06
	3	5.01	4.99	5.06
	4	6.01	6.03	5.99
	5	7.04	7.08	7.03
	6	8.00	7.96	7.97
V_{acid}/μl	1	597.70	996.17	796.22
	2	398.47	487.21	597.70
	3	199.23	298.37	328.59
	4	149.42	149.42	178.45
	5	39.67	49.57	34.70
	6			
V_{base}/μl	1		59.48	
	2	4.96		24.79
	3			
	4	24.79		
	5			
	6	44.61	9.91	29.74

Table A2f. Preparation of samples for adsorption experiments on Lcc raw. Soil fraction f_4. Masses of clay (m), pH and volume of added acid (V_{acid}) and base (V_{base}).

	Sample	Cr	Pb	Cd
m/g	1	0.502	0.500	0.501
	2	0.502	0.500	0.502
	3	0.501	0.502	0.501
	4	0.502	0.501	0.500
	5	0.501	0.500	0.501
	6	0.500	0.502	0.500
pH	1	3.04	2.93	2.93
	2	3.94	3.95	3.96
	3	5.05	5.05	5.06
	4	6.05	6.00	6.06
	5	7.03	7.07	6.99
	6	8.06	8.09	8.06
V_{acid}/µl	1	4980.83	5180.06	5155.15
	2	5080.44	4034.47	4482.74
	3	3875.08	2789.26	3436.77
	4	2241.37	1095.78	1494.25
	5	1344.82	198.28	148.71
	6		14.871	4.96
V_{base}/µl	1			
	2	29.74		
	3			
	4			
	5			
	6		19.83	9.91

Appendix 3: Adsorption data 2

Table A3a. Equilibrium pH and concentration of metals (*c*) in the supernatant for Zmc.

	Sample	Cu	Cr	Pb	Zn	Cd
Equilibrium	1	4.06	3.41	3.81	3.93	4.00
pH	2	4.70	3.67	4.60	4.84	4.65
	3	5.12	3.93	5.05	5.82	6.03
	4	5.65	4.50	5.49	6.22	6.44
	5	6.83	7.28	6.25	6.78	6.81
	6	7.99	7.92	7.27	7.56	7.60
	7		2.61			
	8		2.07			
c/mM	1	0.1777[a]	0.1341[a]	0.0206[c]	0.0037[d]	0.0911[e]
	2	0.1573[a]	0.0988[a]	0.0187[c]	0.0035[d]	0.0881[e]
	3	0.1294[a]	0.2913	0.0165[c]	0.0032[d]	0.0793[e]
	4	0.2238[b]	0.0667	0.0132[c]	0.0030[d]	0.0757[e]
	5	0.0904	0.0026	0.0046[c]	0.0027[d]	0.0693[e]
	6	0.0261	0.0026	0.0004[c]	0.0010[d]	0.0502[e]
	7		0.1405[a]			
	8		0.1437[a]			

[a] The samples were diluted five times.
[b] The sample was diluted one time.
[c] The samples were diluted 40 times.
[d] The samples were diluted 250 times.
[e] The samples were diluted 10 times.

Table A3b. Equilibrium pH and concentration of metals (*c*) in the supernatant for Lcc1.

	Sample	Cr	Pb	Cd
Equilibrium	1	3.83	3.96	3.79
pH	2	4.35	4.60	5.61
	3	4.71	5.12	6.37
	4	5.29	5.58	6.79
	5	6.02	6.39	7.08
	6	7.29	7.41	7.49
c/mM	1	0.1694	0.0073[c]	0.0642[e]
	2	0.1245	0.0041[c]	0.0507[e]
	3	0.0892	0.0029[c]	0.0438[e]
	4	0.0507	0.0021[c]	0.0380[e]
	5	0.0314	0.0013[c]	0.0329[e]
	6	0.0154	0.0009[c]	0.0226[e]

[c] The samples were diluted 40 times.
[e] The samples were diluted 10 times.

Table A3c. Equilibrium pH and concentration of metals (*c*) in the supernatant for Nc2.

	Sample	Cr	Pb	Cd
Equilibrium	1	3.94	3.99	4.06
pH	2	4.36	4.63	4.71
	3	4.77	5.11	5.68
	4	5.28	5.56	6.21
	5	6.04	6.27	6.78
	6	6.87	7.04	7.39
c/mM	1	0.1181	0.0078[c]	0.0548[e]
	2	0.0988	0.0053[c]	0.0497[e]
	3	0.0731	0.0035[c]	0.0410[e]
	4	0.0443	0.0024[c]	0.0385[e]
	5	0.0250	0.0013[c]	0.0336[e]
	6	0.0154	0.0006[c]	0.0266[e]

[c] The samples were diluted 40 times.
[e] The samples were diluted 10 times.

Table A3d. Equilibrium pH and concentration of metals (*c*) in the supernatant for Nc raw.

	Sample	Cr	Pb	Cd
Equilibrium	1	4.26	3.77	4.24
pH	2	5.53	5.96	6.81
	3	6.92	6.94	7.57
	4	7.32	7.62	7.47
	5	7.76	8.16	7.63
	6	8.09	8.16	7.58
c/mM	1	0.0603	0.0051[c]	0.0580[e]
	2	0.0379	0.0006[c]	0.0405[e]
	3	0.0250	0.0003[c]	0.0234[e]
	4	0.0218	0.0004[c]	0.0172[e]
	5	0.0218	0.0003[c]	0.0116[e]
	6	0.0218	0.0006[c]	0.0079[e]

[c] The samples were diluted 40 times.
[e] The samples were diluted 10 times.

Table A3e. Equilibrium pH and concentration of metals (*c*) in the supernatant for Lcc raw.

	Sample	Cr	Pb	Cd
Equilibrium	1	5.48	5.34	4.71
pH	2	5.01	6.52	6.45
	3	7.56	6.96	6.71
	4	7.81	7.83	7.09
	5	8.02	8.21	7.61
	6	8.42	8.33	7.97
c/mM	1	0.0186	0.0016[c]	0.0503[e]
	2	0.0186	0.0003[c]	0.0371[e]
	3	0.0090	0.0001[c]	0.0329[e]
	4	0.0154	0.0000[c]	0.0227[e]
	5	0.0218	0.0000[c]	0.0099[e]
	6	0.0186	0.0000[c]	0.0058[e]

[c] The samples were diluted 40 times.
[e] The samples were diluted 10 times.

Appendix 4: Energy dispersive spectrometer (EDS) results

Figs. A4a-A4i show spectrums from EDS analyses and weight percent of detectable elements in the different samples. Keep in mind that the machine (Hitachi TM-1000) only detects sodium and heavier elements. All analyses were performed on an area of the samples at 3000-4000 magnification. Spot is the alternative choice where a specific particle is analyzed. The following acquisition conditions and quantification settings were used:

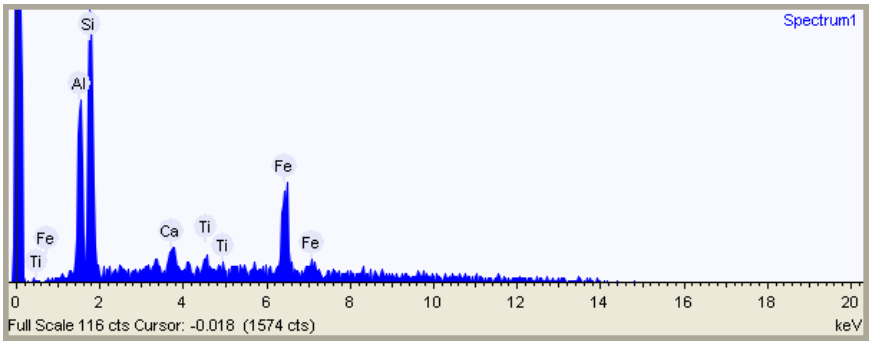
Acquisition conditions

Acquisition time (s)	60.0 (90.0 for Lcc1, Lcc2 and Zmc)
Process time	4
Accelerating voltage (kV)	15.0

Quantification Settings

Quantification method	All elements (normalized)

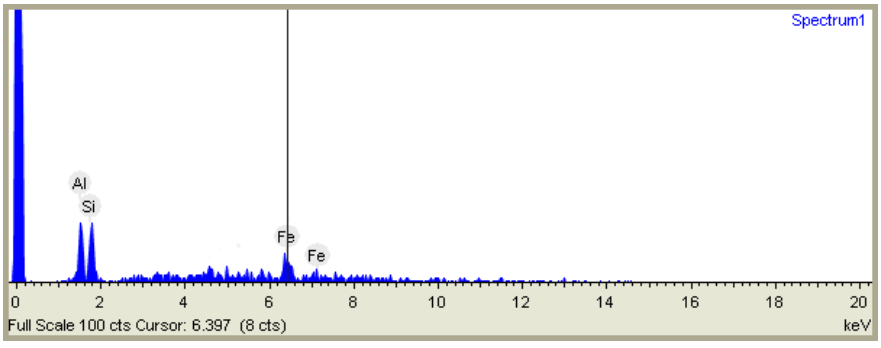
Figure A4a. Nc raw x3000 area



Summary results

Element	Weight %
Aluminum, Al	19.2
Silicon, Si	29.8
Calcium, Ca	3.4
Titanium, Ti	2.9
Iron, Fe	44.7

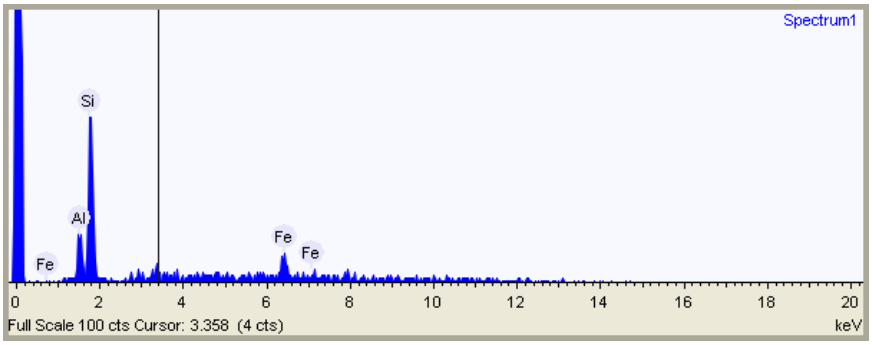
Figure A4b. Nc1 x3000 area



Summary results

Element	Weight %
Aluminum, Al	28.2
Silicon, Si	32.7
Iron, Fe	39.1

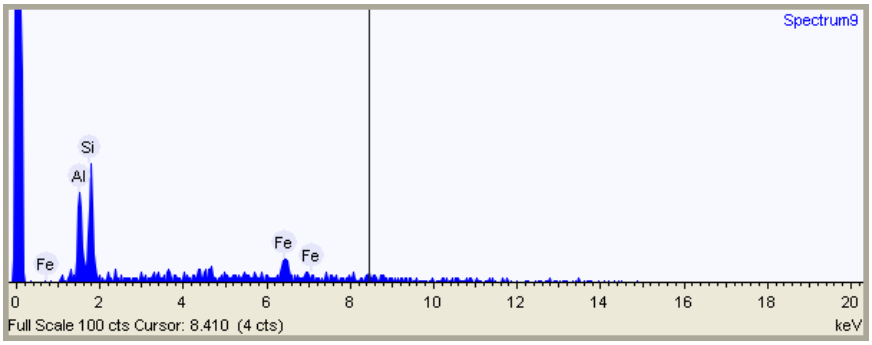
Figure A4c. Nc2 x4000 area



Summary results

Element	Weight %
Aluminum, Al	13.6
Silicon, Si	52.2
Iron, Fe	34.2

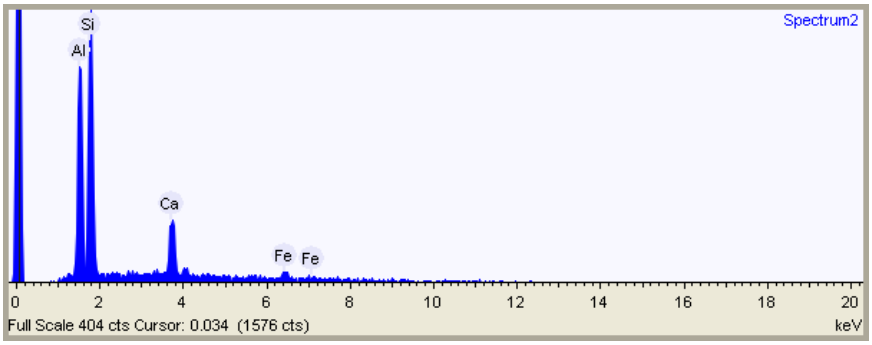
Figure A4d. Nc3 x3000 area



Summary results

Element	Weight %
Aluminum, Al	27.5
Silicon, Si	37.2
Iron, Fe	35.3

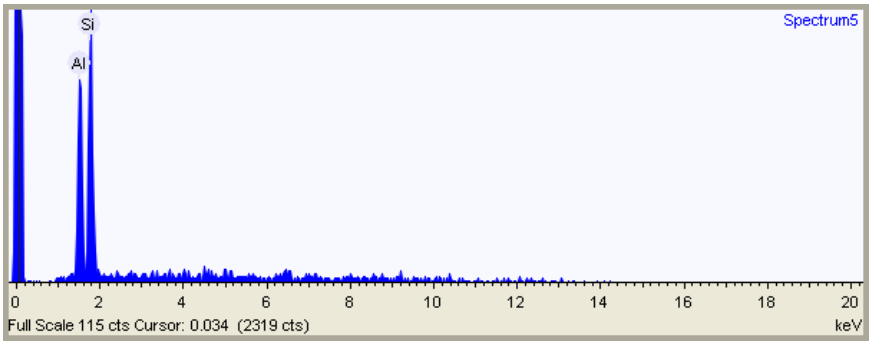
Figure A4e. Lcc raw x3000 area



Summary results

Element	Weight %
Aluminum, Al	29.2
Silicon, Si	47.7
Calcium, Ca	17.2
Iron, Fe	5.9

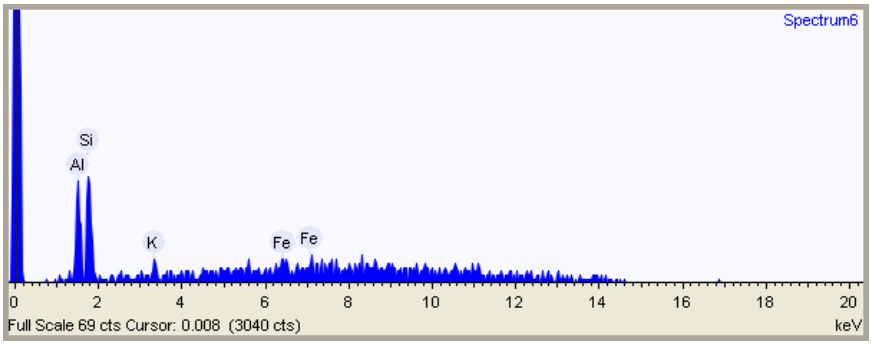
Figure A4f. Lcc1 x3000 area



Summary results

Element	Weight %
Aluminum, Al	35.5
Silicon, Si	64.5

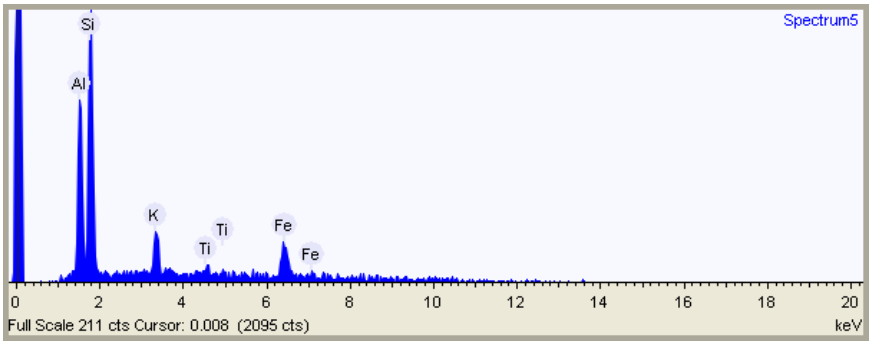
Figure A4g. Lcc2 x3000 area



Summary results

Element	Weight %
Aluminum, Al	29.1
Silicon, Si	41.7
Potassium, K	8.4
Iron, Fe	20.9

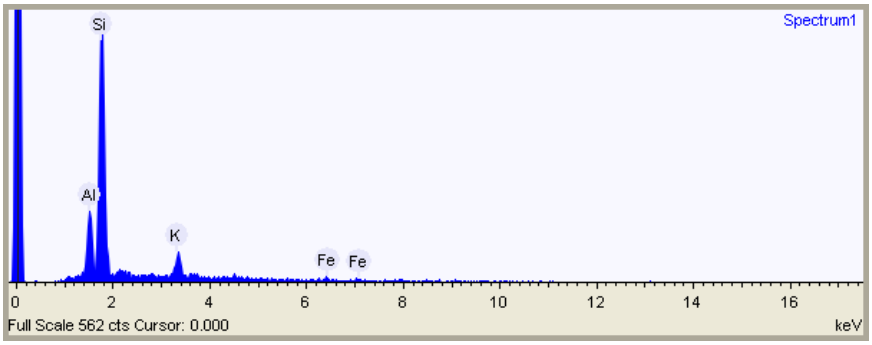
Figure A4h. Zmc raw x3000 area



Summary results

Element	Weight %
Aluminum, Al	22.1
Silicon, Si	39.9
Potassium, K	10.1
Titanium, Ti	2.7
Iron, Fe	25.2

Figure A4i. Zmc x4000 area



Summary results

Element	Weight %
Aluminum, Al	14.5
Silicon, Si	70.4
Potassium, K	10.9
Iron, Fe	4.1

Appendix 5: Titration plots

In Figs. A5a–A5p, measured equilibrium pH level is plotted against volume of added nitric acid and sodium hydroxide, respectively, for the different soil samples.

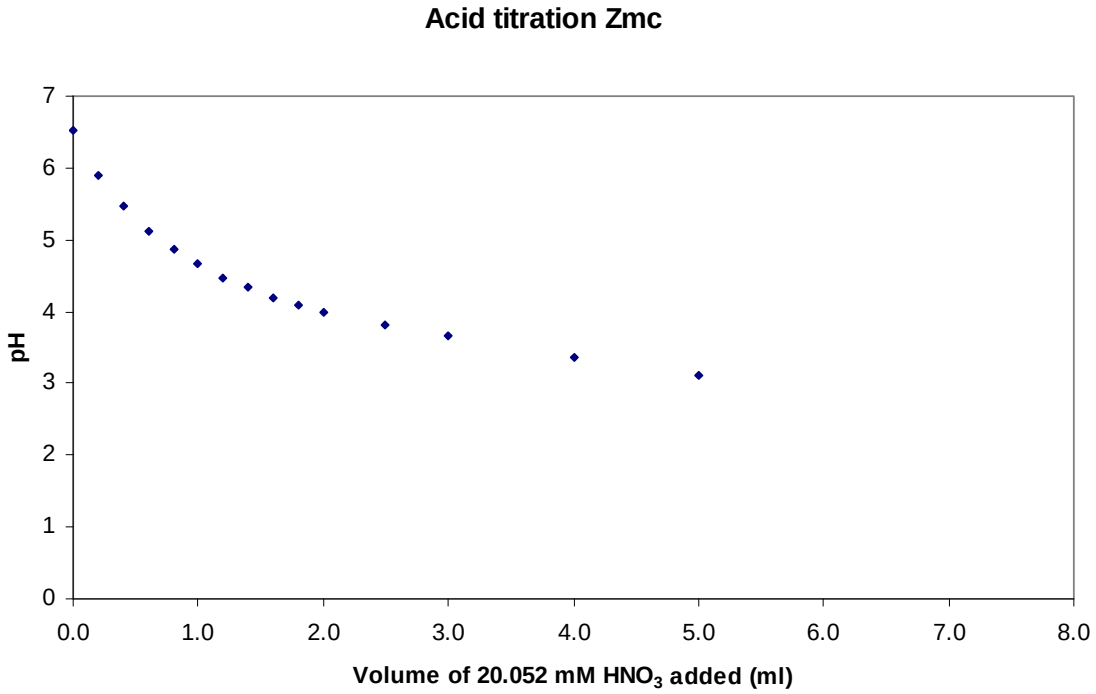


Figure A5a. Acid titration plot for Zmc.

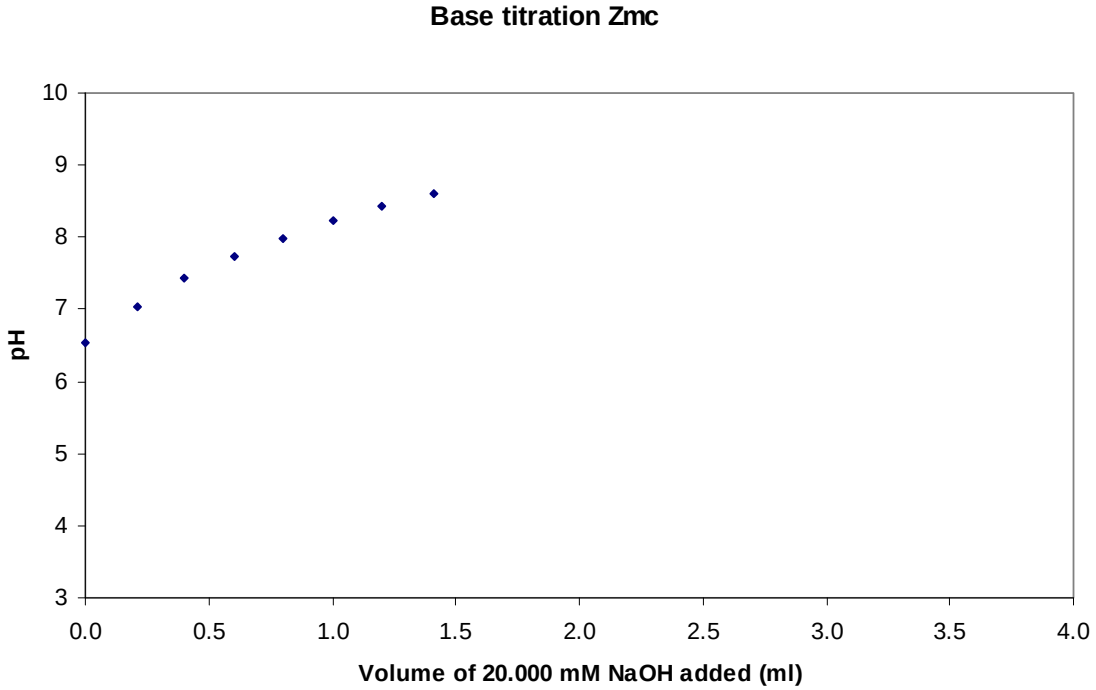


Figure A5b. Base titration plot for Zmc.

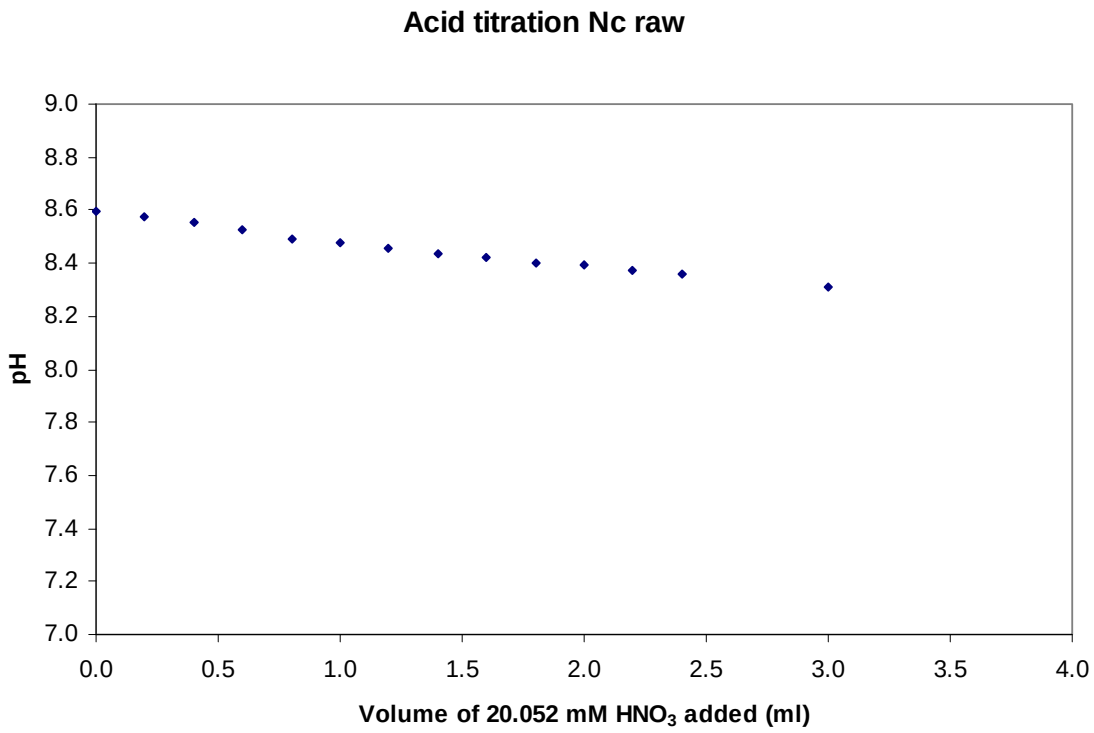


Figure A5c. Acid titration plot for Nc raw.

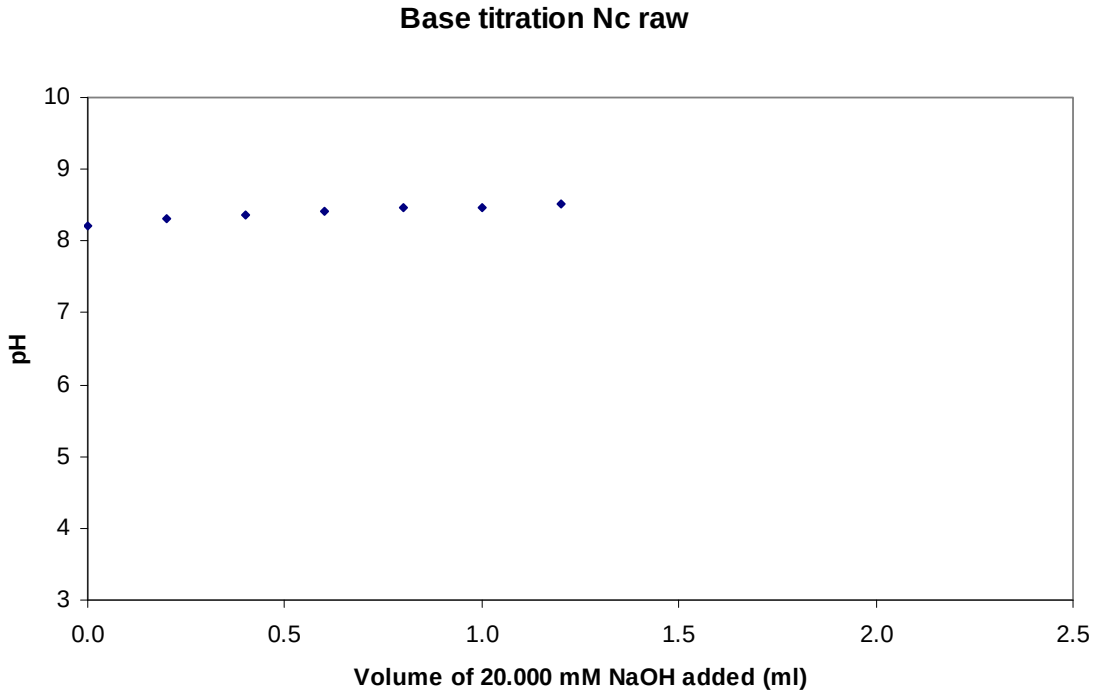


Figure A5d. Base titration plot for Nc raw.

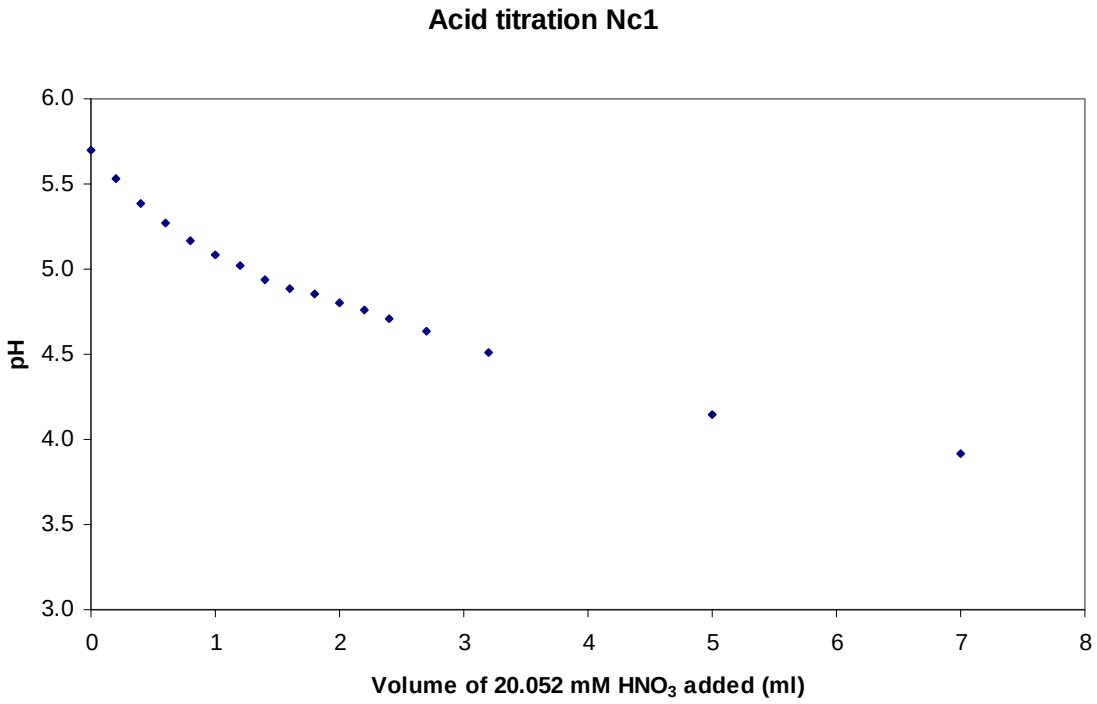


Figure A5e. Acid titration plot for Nc1.

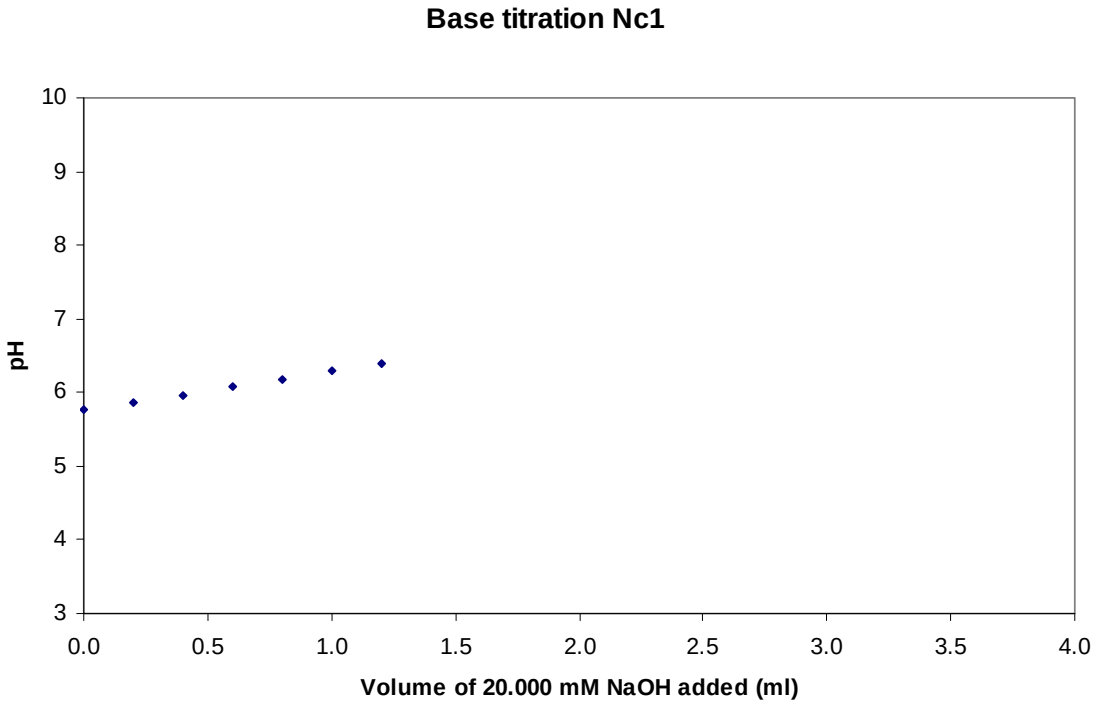


Figure A5f. Base titration plot for Nc1.

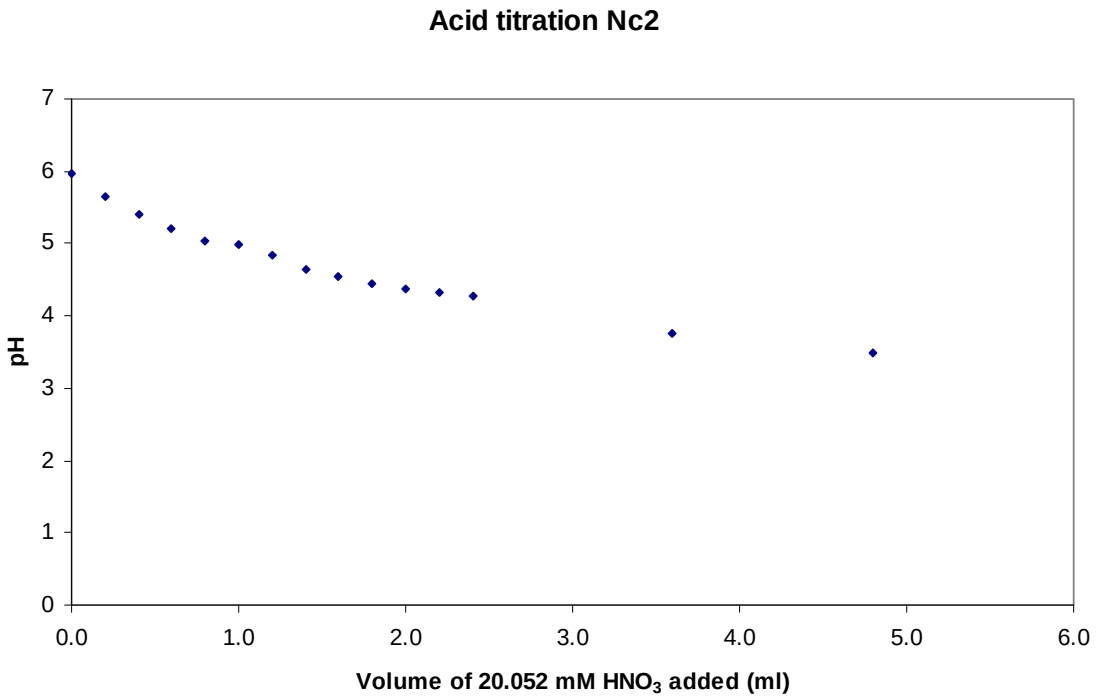


Figure A5g. Acid titration plot for Nc2.

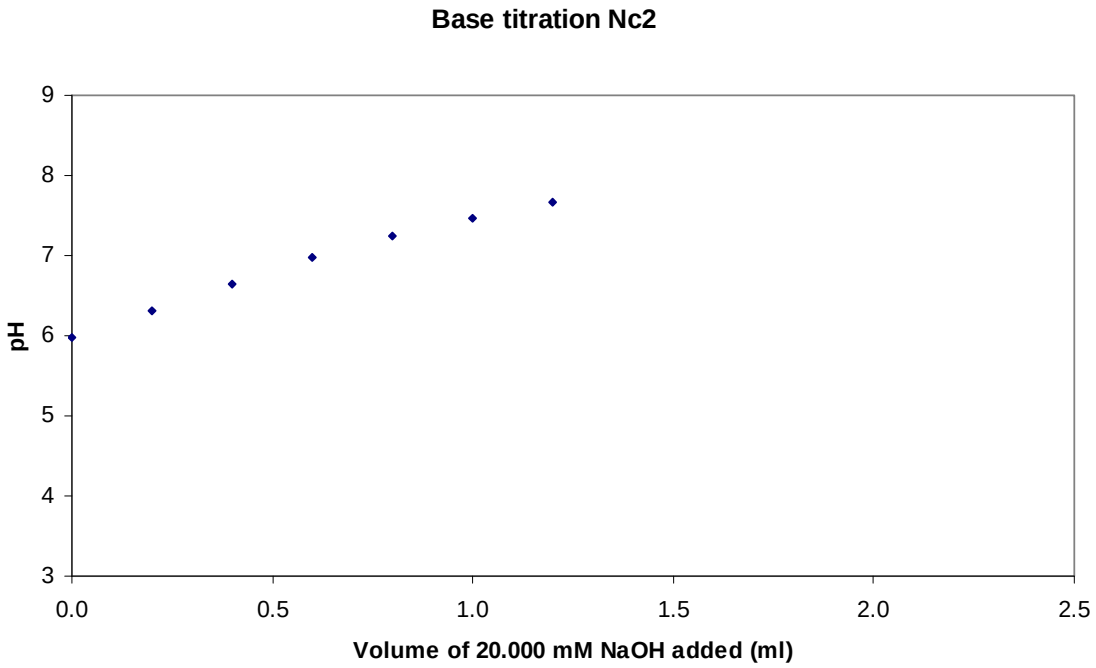


Figure A5h. Base titration plot for Nc2.

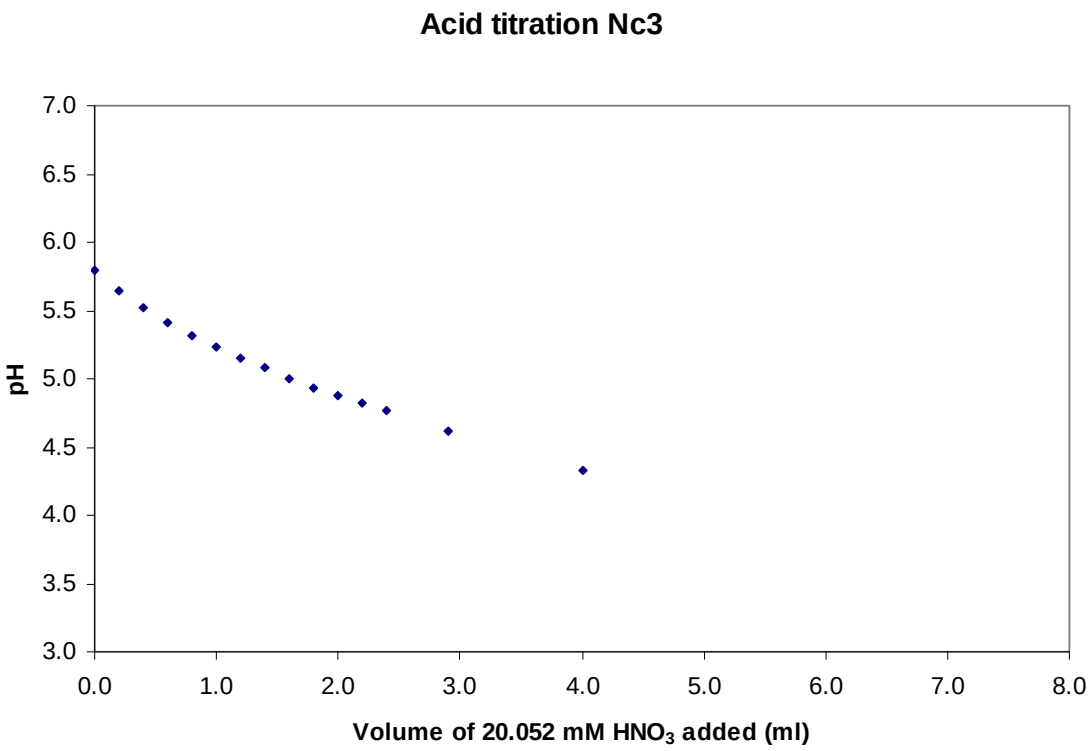


Figure A5i. Acid titration plot for Nc3.

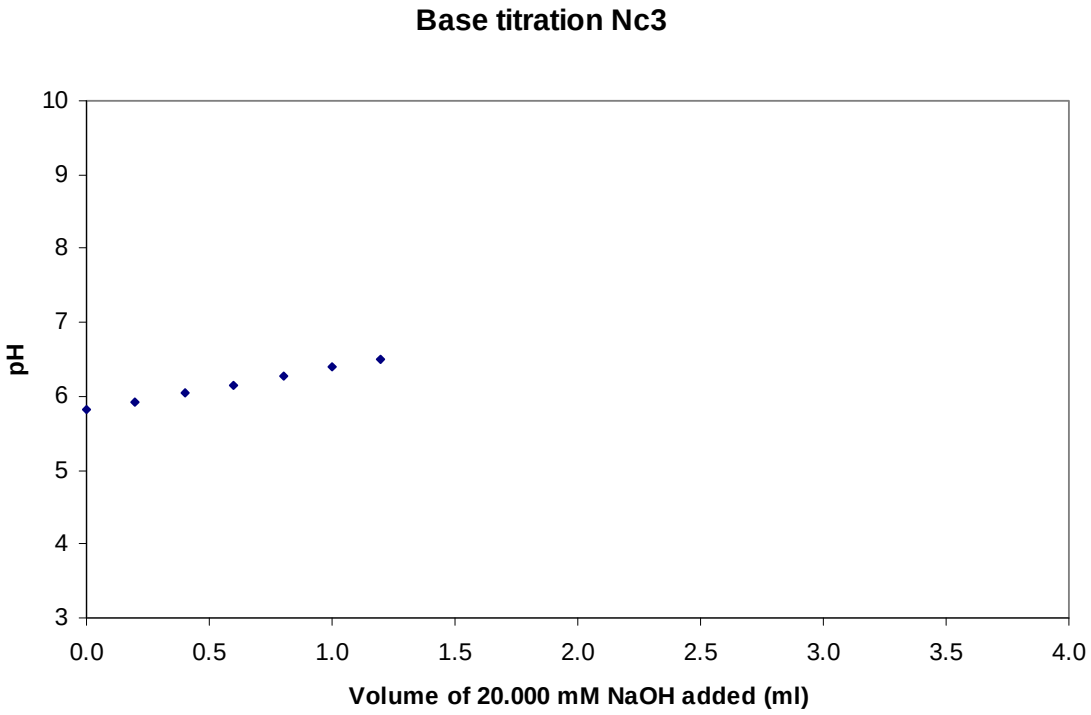


Figure A5j. Base titration plot for Nc3.

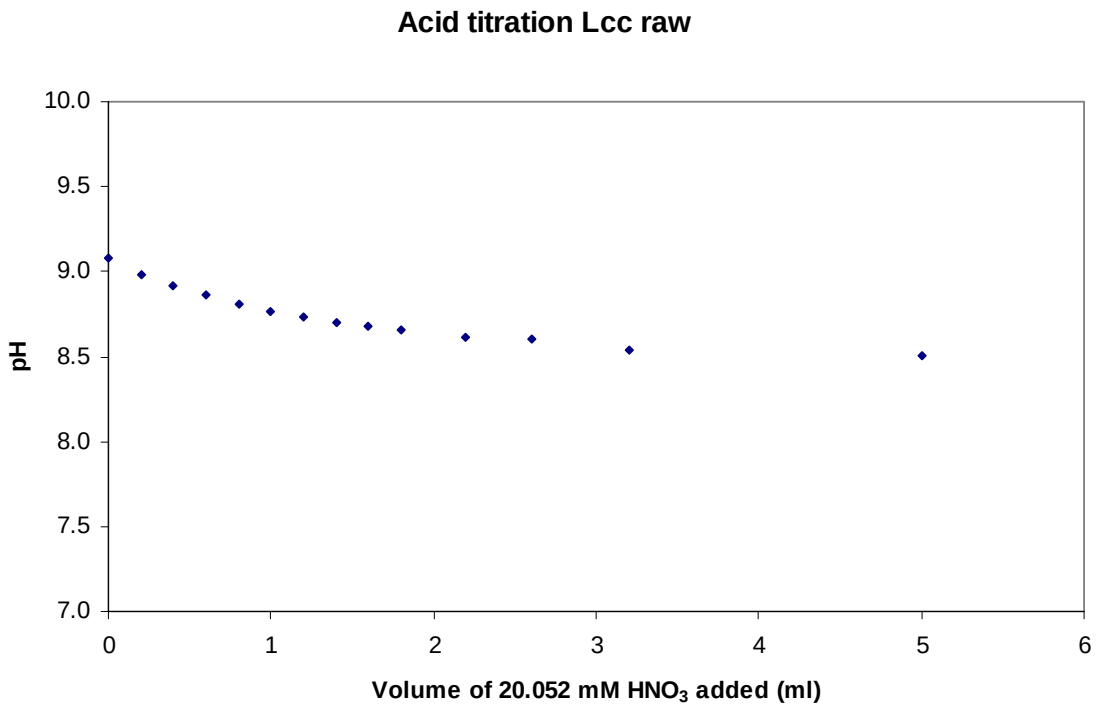


Figure A5k. Acid titration plot for Lcc raw.

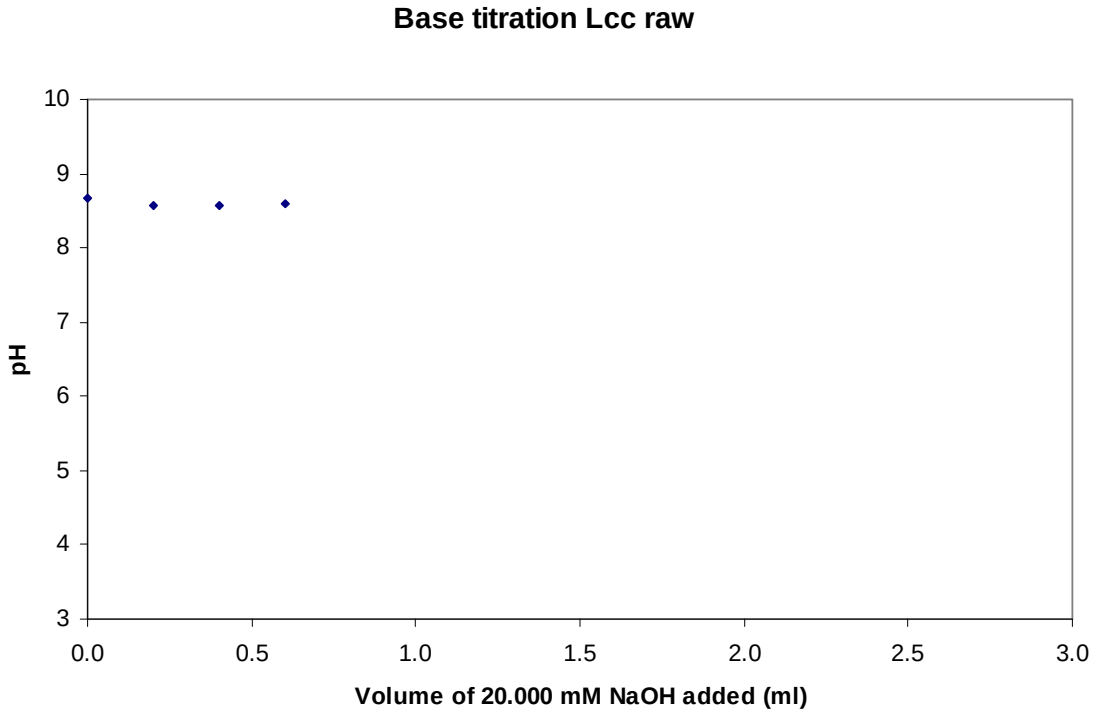


Figure A5l. Base titration plot for Lcc raw.

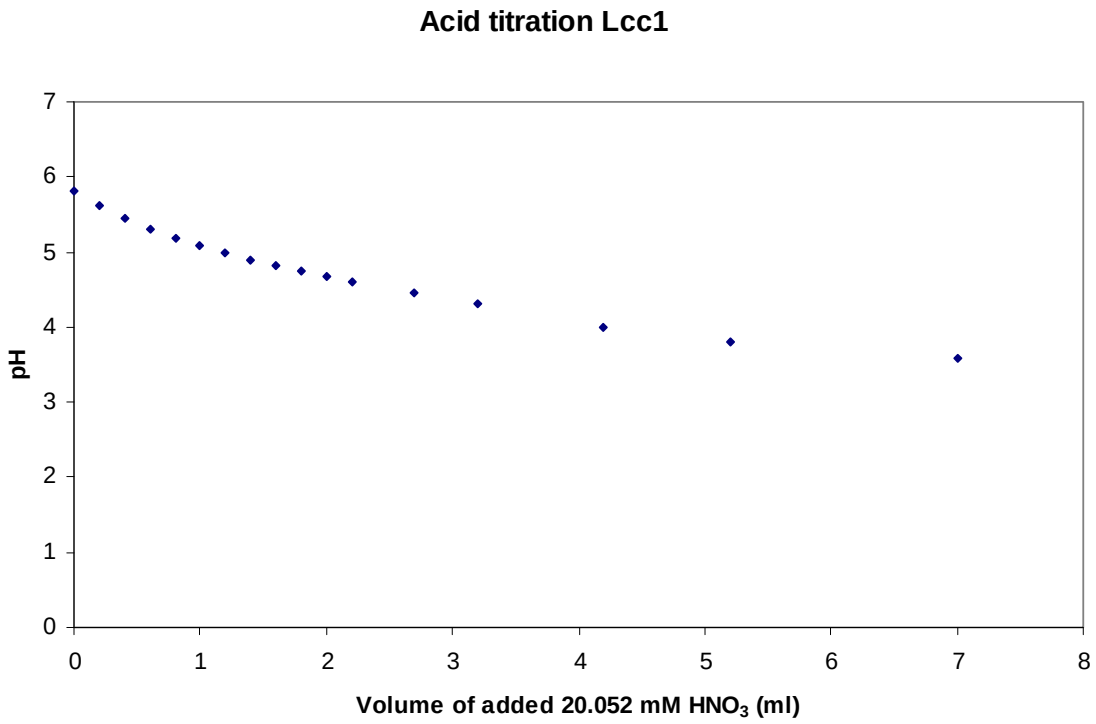


Figure A5m. Acid titration plot for Lcc1.

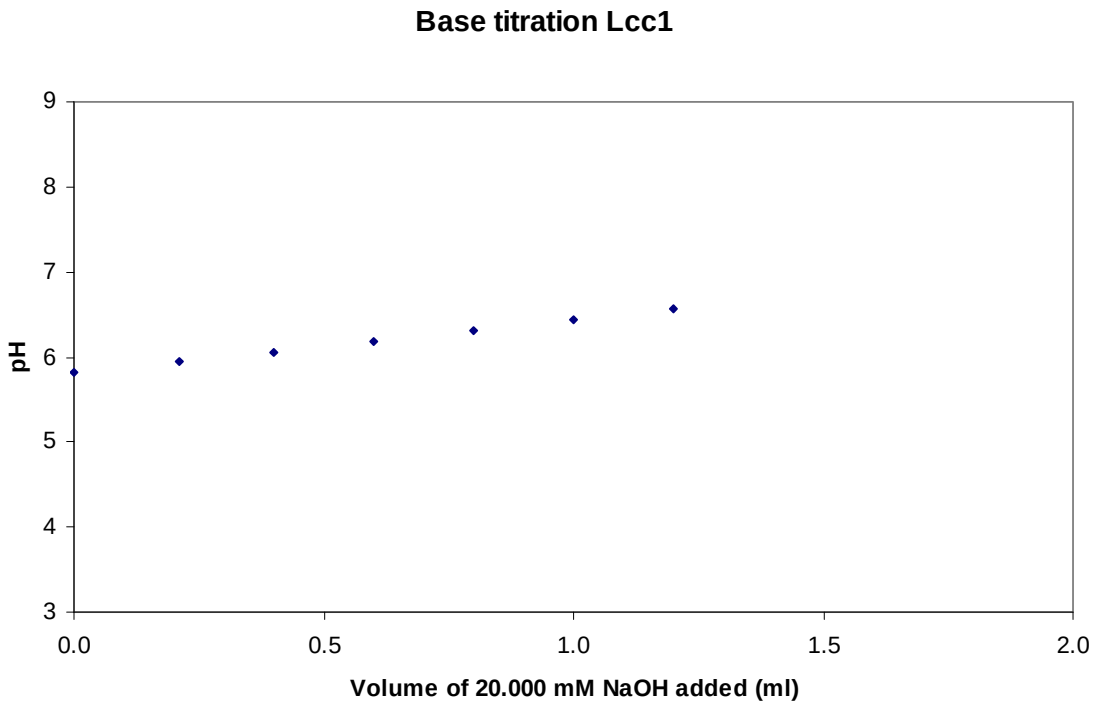


Figure A5n. Base titration plot for Lcc1.

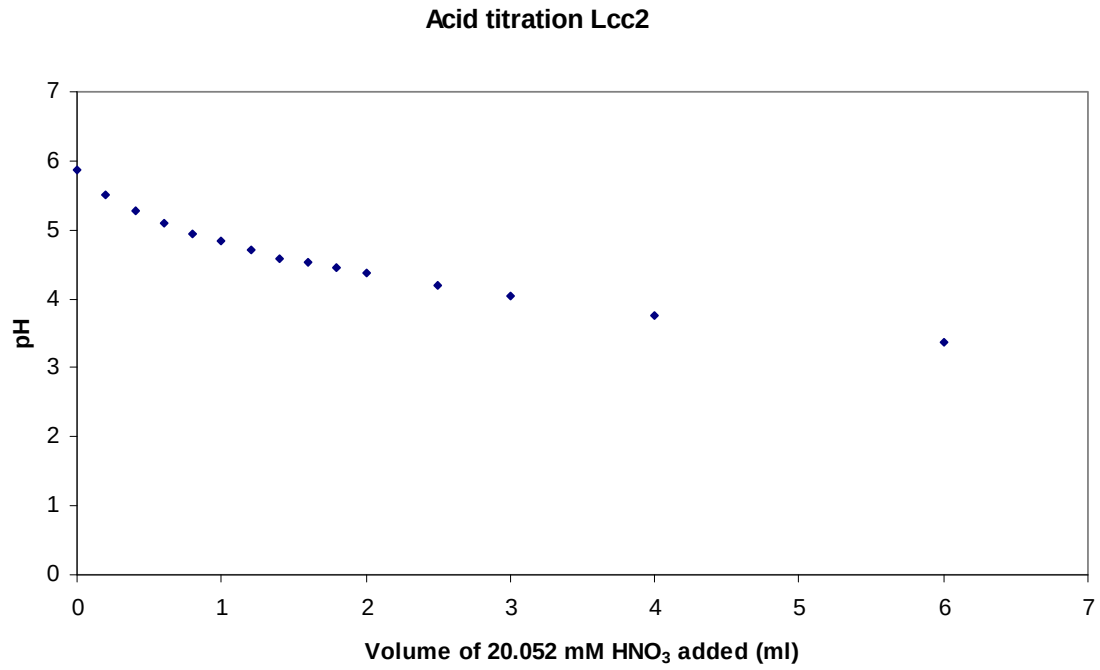


Figure A5o. Acid titration plot for Lcc2.

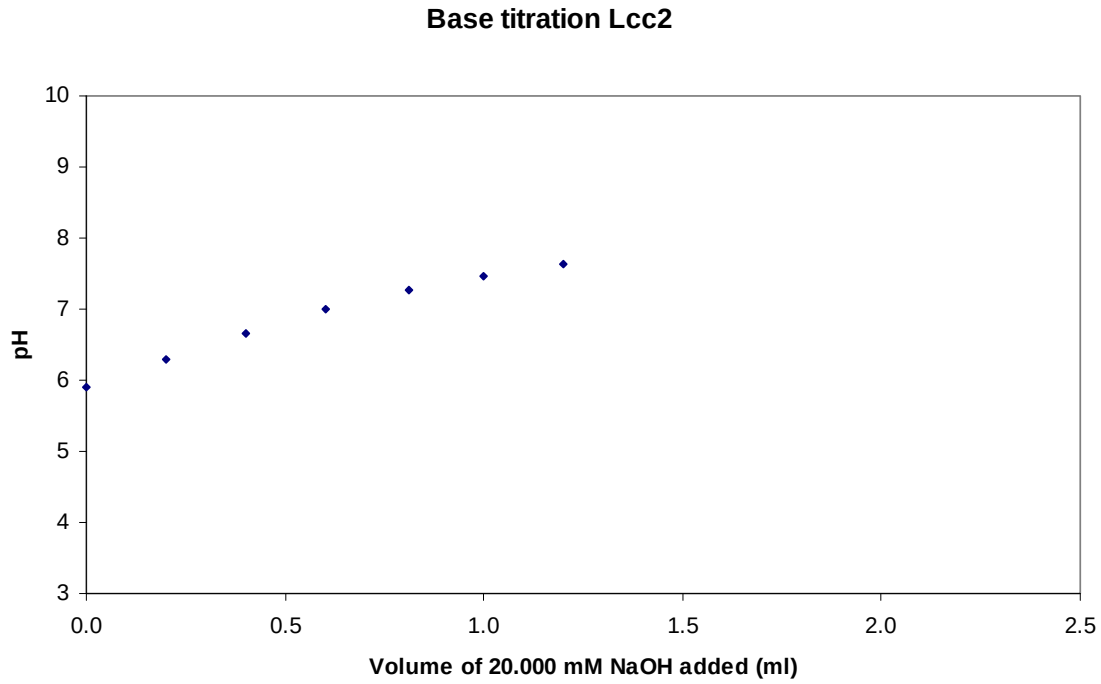


Figure A5p. Base titration plot for Lcc2.

Appendix 6: pK_a plots

Figs. A6a–A6g illustrate how pK_a vary with charge density, Z, for the different soils. $pK^{s}_{a1,intr}$, $pK^{s}_{a2,intr}$ and pH_{pznpc} values are written in the figure texts.

Due to an unknown reason, the pK_a values nearest $Z = 0$ differ from the trend that the other points create. These pK_a values are marked with a white background in the graphs and are not included when creating the regression lines, even though their presence would not influence the pH_{pznpc} values significantly.

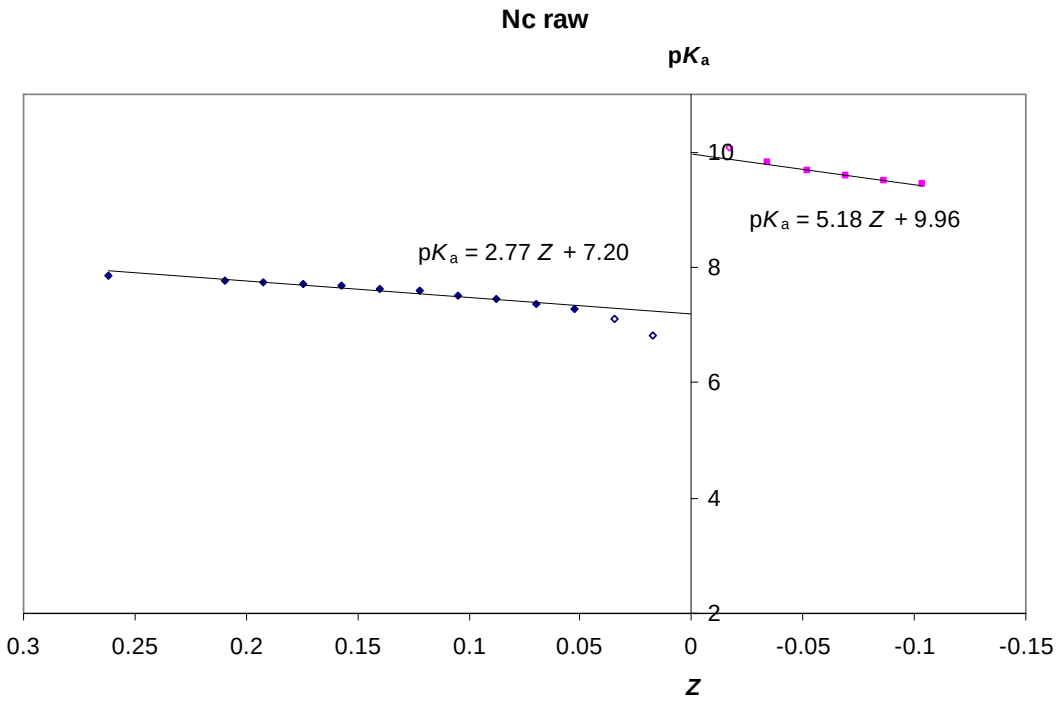


Figure A6a. The negative logarithmic form of the acidity constant, pK_a, plotted against charge density, Z, for Nc raw. $pK^{s}_{a1,intr}$ = 7.20, $pK^{s}_{a2,intr}$ = 9.96, pH_{pznpc} = 8.58.

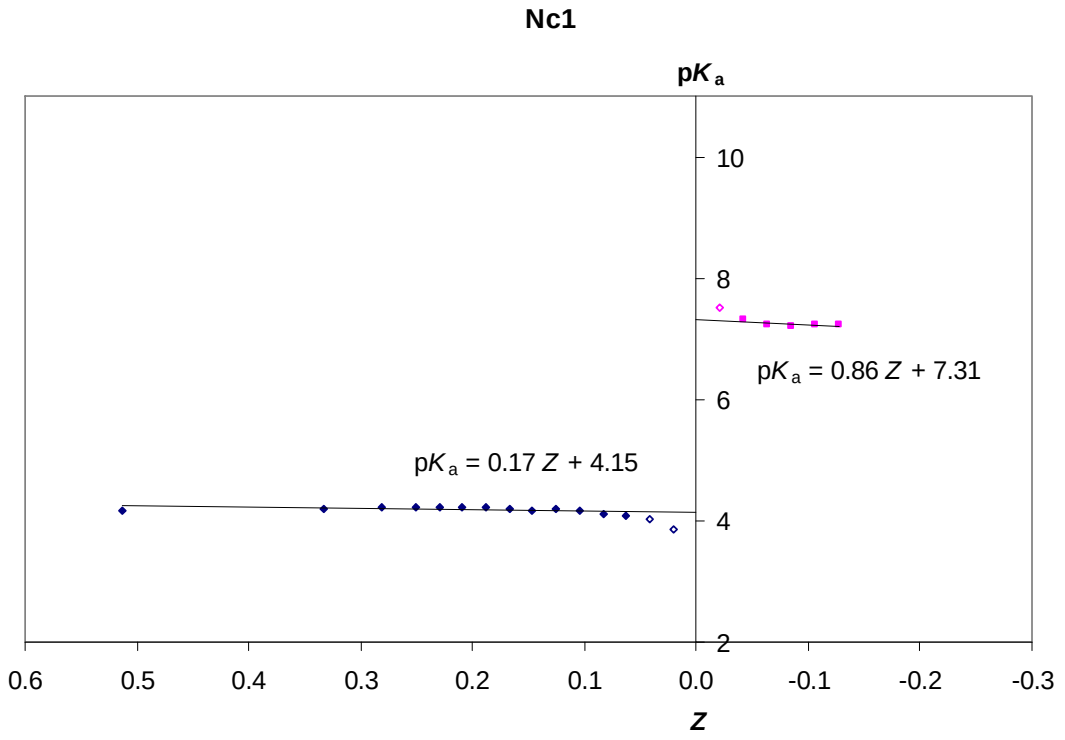


Figure A6b. The negative logarithmic form of the acidity constant, pK_a, plotted against charge density, Z, for Nc1. $pK^{s}_{a1,intr}$ = 4.15, $pK^{s}_{a2,intr}$ = 7.31, pH_{pznpc} = 5.73.

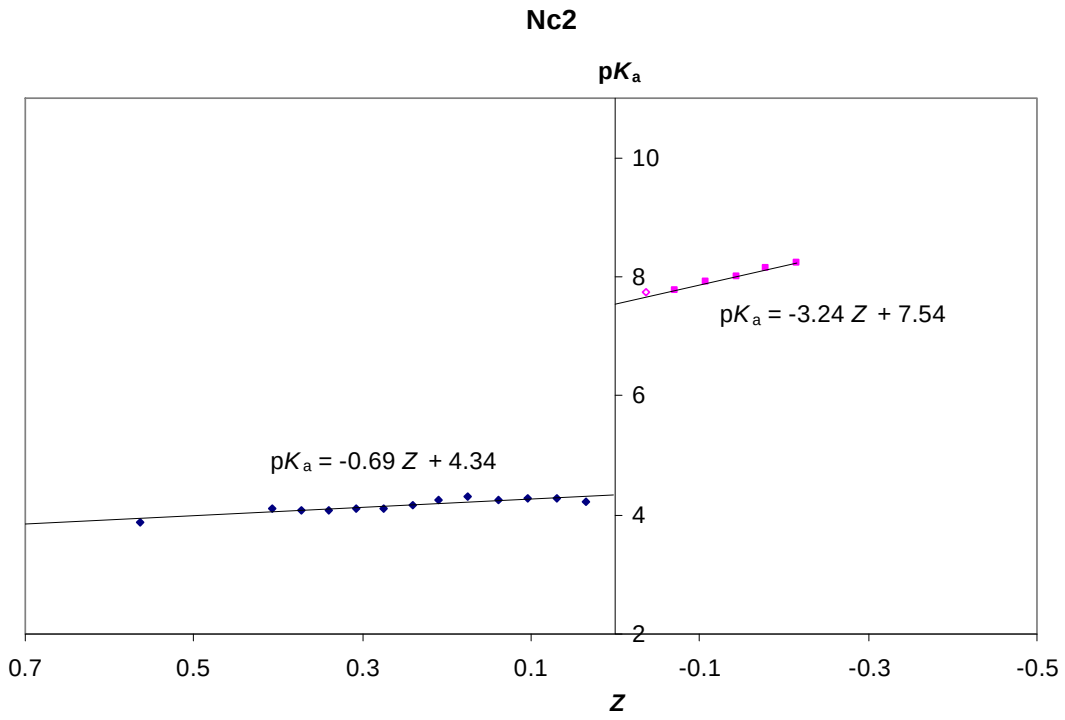


Figure A6c. The negative logarithmic form of the acidity constant, pK_a, plotted against charge density, Z, for Nc2. p$K^s_{a1,intr}$ = 4.34, p$K^s_{a2,intr}$ = 7.54, pH_{pznpc} = 5.94.

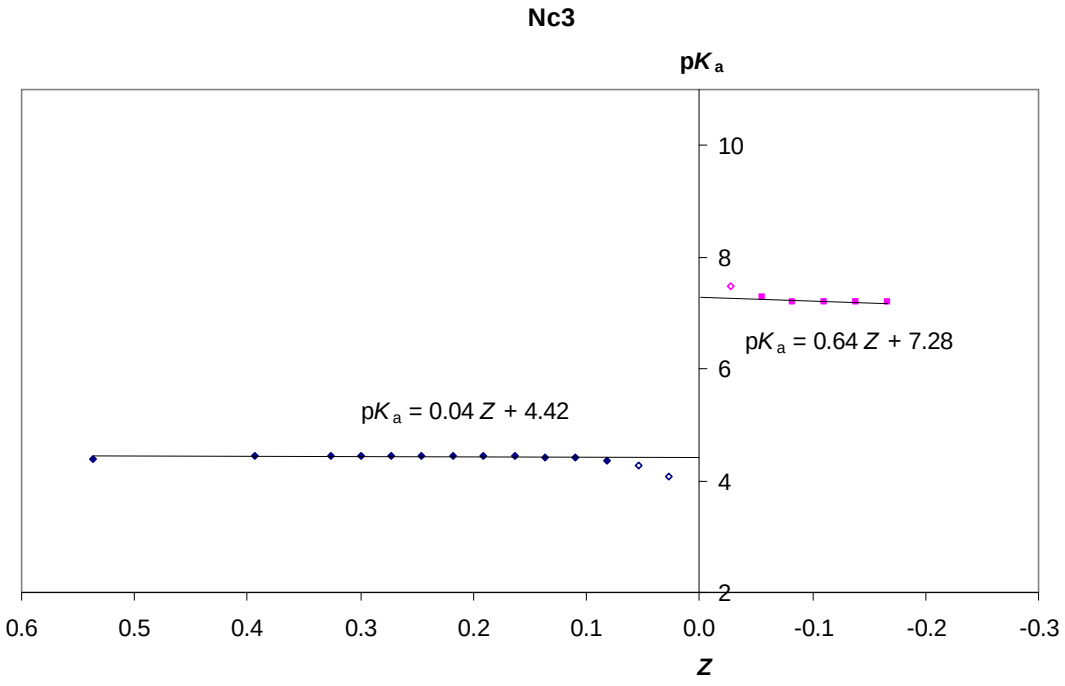


Figure A6d. The negative logarithmic form of the acidity constant, pK_a, plotted against charge density, Z, for Nc3. p$K^s_{a1,intr}$ = 4.42, p$K^s_{a2,intr}$ = 7.28, pH_{pznpc} = 5.85.

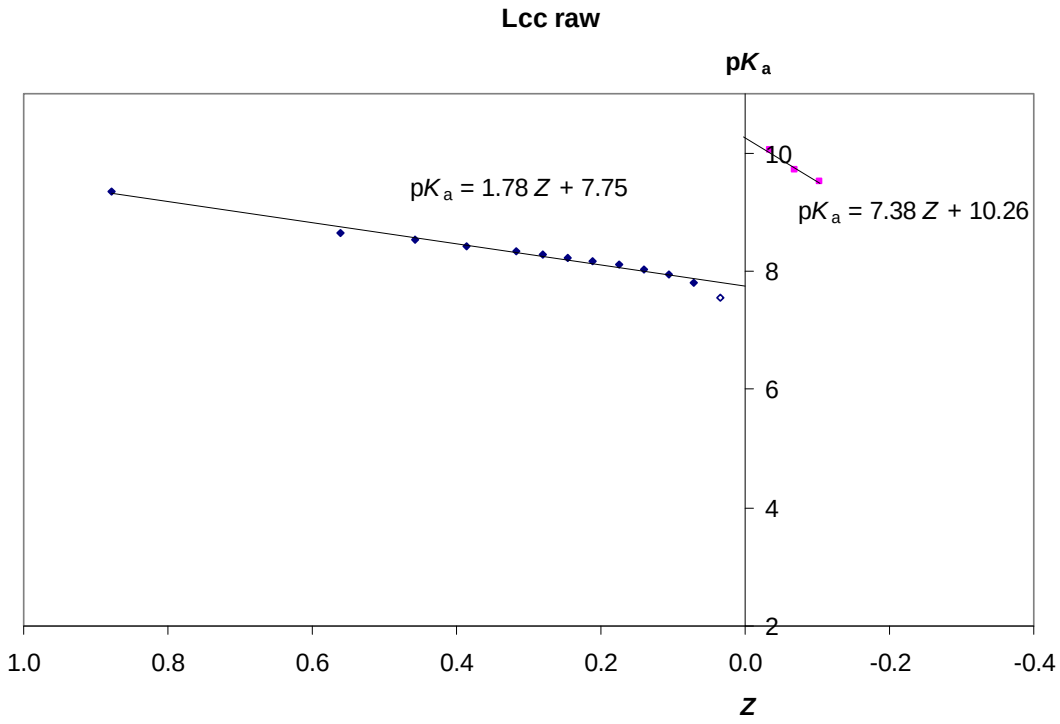


Figure A6e. The negative logarithmic form of the acidity constant, pK_a, plotted against charge density, Z, for Lcc raw. $pK^{s}_{a1,intr}$ = 7.75, $pK^{s}_{a2,intr}$ = 10.26, pH_{pznpc} = 9.00.

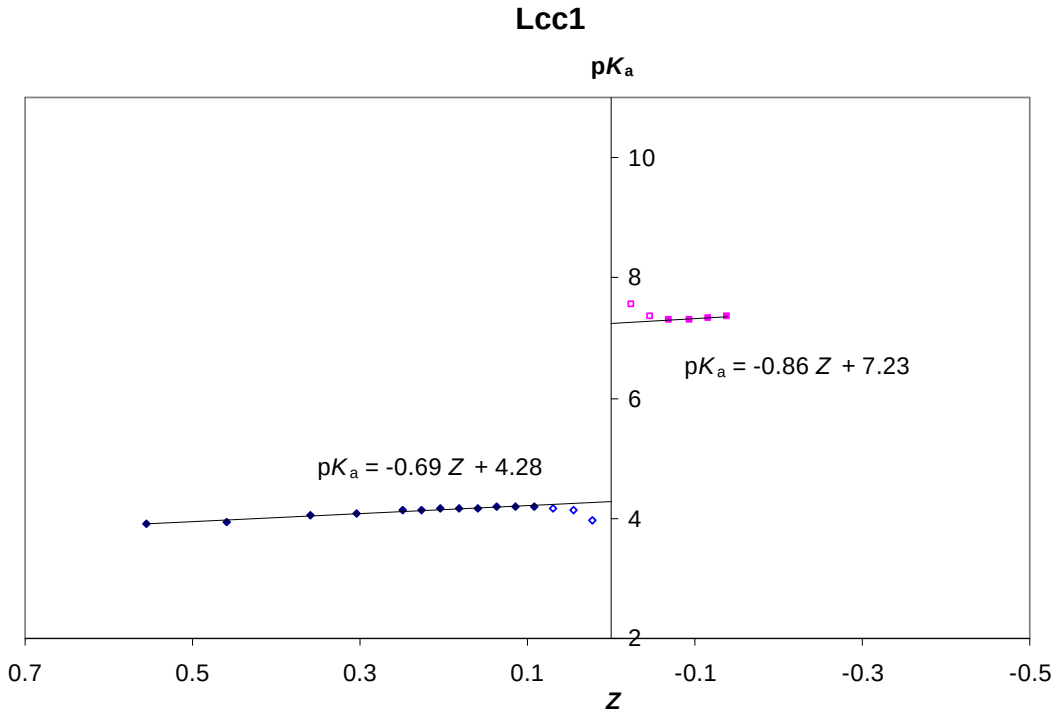


Figure A6f. The negative logarithmic form of the acidity constant, pK_a, plotted against charge density, Z, for Lcc1. $pK^{s}_{a1,intr}$ = 4.28, $pK^{s}_{a2,intr}$ = 7.23, pH_{pznpc} = 5.76.

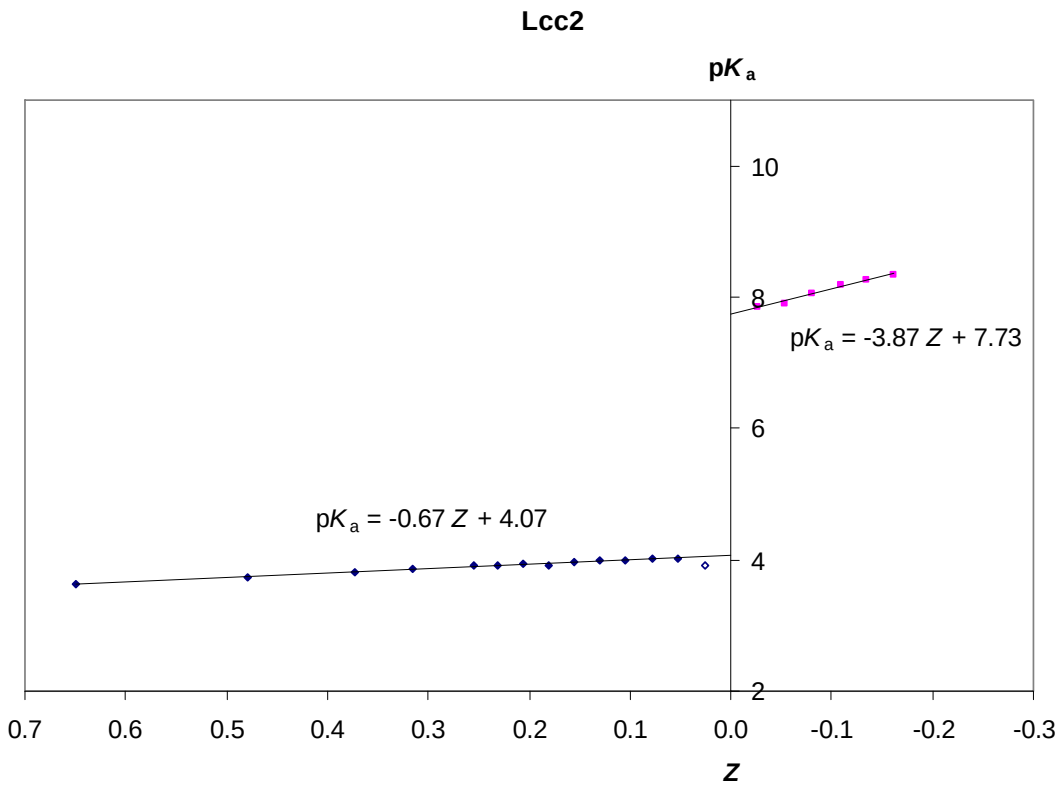


Figure A6g. The negative logarithmic form of the acidity constant, pK_a, plotted against charge density, Z, for Lcc2. $pK^{s}_{a1,intr}$ = 4.07, $pK^{s}_{a2,intr}$ = 7.73, pH_{pznpc} = 5.90.